

PhD Thesis

School of Chemistry

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The application of Cs-exchanged tungstophosphoric acid as an additive in the direct synthesis of hydrogen peroxide and the use of Au-Pd / TS-1 in a one-pot approach to cyclohexanone oxime production.

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## Summary.

The work presented within this thesis can be separated into two distinct parts. The first investigates the direct synthesis of hydrogen peroxide from molecular hydrogen and oxygen using gold-palladium supported catalysts and caesium exchanged tungstophosphoric acid as an acidic additive. The direct synthesis of  $\text{H}_2\text{O}_2$  presents an environmentally friendly alternative to the current industrial, anthraquinone process. However for the direct route to be viable a variety of issues must be addressed. Primarily catalytic selectivity towards  $\text{H}_2\text{O}_2$  is a major concern for the majority of catalysts active for  $\text{H}_2\text{O}_2$  synthesis, with the degradation of  $\text{H}_2\text{O}_2$  through hydrogenation or decomposition reported for a number of catalysts within the literature.

The use of acid either during catalyst preparation or as part of the reaction solution has previously been shown to improve selectivity towards  $\text{H}_2\text{O}_2$ . Furthermore acidic supports, including heteropolyacid, have been observed to produce catalysts with greater selectivity than those with a higher isoelectric point and in turn provide higher yields of  $\text{H}_2\text{O}_2$ . This work investigates the ability of caesium exchanged heteropolyacids to improve catalytic activity towards  $\text{H}_2\text{O}_2$  when used in addition to Au-Pd supported catalysts, in particular 2.5 wt. % Au – 2.5 wt. Pd /  $\text{TiO}_2$ .

The second part of this work is concerned with the ammoximation of cyclohexanone to cyclohexanone oxime via the *in-situ* formation of  $\text{H}_2\text{O}_2$ , in a one-pot style process. The conditions associated with ammoximation of cyclohexanone that is the presence of elevated temperatures and basic conditions, are considered extremely harsh for  $\text{H}_2\text{O}_2$  stability. The *in-situ* generation of  $\text{H}_2\text{O}_2$  during the ammoximation of cyclohexanone to cyclohexanone oxime would yield significant reductions in overall costs of the ammoximation reaction. Primarily these costs are associated with the purchasing, transport, storage and dilution of  $\text{H}_2\text{O}_2$ . This work determines the feasibility of a one-pot ammoximation process via *in-situ*  $\text{H}_2\text{O}_2$  formation. Firstly, reaction conditions are established for this process and following this the role of catalyst design in improving selectivity towards cyclohexanone oxime as well as cyclohexanone conversion for this reaction is studied.

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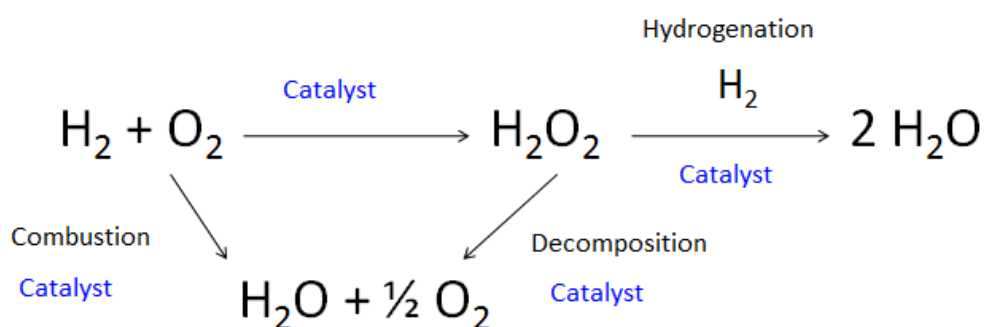
# 1. Introduction.

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## 1.1 Overview.

The vast majority of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) produced globally is done so *via* the indirect or anthraquinone auto-oxidation (AO) process, which involves the hydrogenation of an alkyl anthraquinone which is subsequently oxidised. This process has been continually improved since it was first developed in 1939 by Riedel and Pfleiderer<sup>1</sup> and so is highly energy efficient. Although problems of scale and the environmentally unfriendly nature of solvent systems used present a considerable downside to the indirect process.

The direct synthesis of  $\text{H}_2\text{O}_2$  has been a challenge for the scientific community for over 100 years, with the first patent, for a Pd catalyst, filed in 1914<sup>2</sup> and until recently investigation into the catalysis of the direct route have been based upon Pd catalysts.<sup>3-7</sup> Figure 1.1 shows the synthesis route for  $\text{H}_2\text{O}_2$  as well as the sequential hydrogenation / decomposition steps. It is known that catalysts active towards the synthesis of  $\text{H}_2\text{O}_2$  are almost always active towards its subsequent break down and it is these side reactions that result in a loss of catalytic selectivity and therefore reduce the net formation of  $\text{H}_2\text{O}_2$ . Although it has been reported recently that catalyst design can be modified in order to limit or even inhibit these subsequent reactions.<sup>8-10</sup>



**Figure 1.1** The direct synthesis of  $\text{H}_2\text{O}_2$  and its subsequent degradation pathways.

The issue of catalyst selectivity can be understood as the formation of water from  $\text{H}_2$  and  $\text{O}_2$  is thermodynamically favorable, in comparison to the formation of  $\text{H}_2\text{O}_2$  as summarized by Equations 1-2.



1.  $\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}_2(\text{l}) \quad \Delta G_{298} = -120.5 \text{ kJ/mol}$
2.  $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}_2(\text{l}) \quad \Delta G_{298} = -237.2 \text{ kJ/mol}$

Furthermore the undesired subsequent  $\text{H}_2\text{O}_2$  decomposition and hydrogenation reactions are also thermodynamically favorable:

3.  $\text{H}_2\text{O}_2(\text{l}) \rightarrow \text{H}_2\text{O}(\text{l}) + \frac{1}{2} \text{O}_2(\text{g}) \quad \Delta G_{298} = -116.7 \text{ kJ/mol}$
4.  $\text{H}_2\text{O}_2(\text{l}) + \text{H}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) \quad \Delta G_{298} = -354.0 \text{ kJ/mol}$

The direct synthesis of  $\text{H}_2\text{O}_2$ , therefore demonstrates the need for catalyst design to balance selectivity and activity carefully, as well as the selection of reaction conditions that inhibit the degradation of  $\text{H}_2\text{O}_2$ . It is known that  $\text{H}_2\text{O}_2$  is highly unstable at high temperatures or in the presence of basic conditions<sup>11</sup>. It can be demonstrated that through the use of low reaction temperatures it is possible to limit the thermodynamic favorability of the subsequent  $\text{H}_2\text{O}_2$  degradation reactions. By decreasing temperature it is possible to decrease the entropic contribution to the Gibbs free energy ( $\Delta G$ ), which clearly favors the degradation of  $\text{H}_2\text{O}_2$  to  $\text{H}_2\text{O}$ .

As discussed above the use of Pd as a catalyst for the direct synthesis of  $\text{H}_2\text{O}_2$  has been highly reported. Hutchings' seminal study<sup>12</sup> showed that catalysts containing Au also had some activity towards  $\text{H}_2\text{O}_2$  synthesis, however the crucial finding was that bimetallic Au-Pd supported catalysts were significantly more effective than either monometallic Au or Pd catalyst for the direct synthesis of  $\text{H}_2\text{O}_2$ .<sup>13</sup> Subsequent work by Hutchings and co-workers has shown this to be true on a variety of supports, including  $\text{Al}_2\text{O}_3$ <sup>12</sup>,  $\text{Fe}_2\text{O}_3$ <sup>13</sup>,  $\text{SiO}_2$ <sup>14</sup> and  $\text{TiO}_2$ <sup>15</sup> and where the addition of Au to Pd improves catalytic selectivity and enhances the rate of  $\text{H}_2\text{O}_2$  synthesis.

Various studies have shown that supports with lower isoelectric points, effectively more acidic supports<sup>16, 17</sup>, such as carbon as well as the addition of acid additives including  $\text{HCl}$ <sup>18</sup>,  $\text{H}_3\text{PO}_4$ <sup>19</sup> and  $\text{H}_2\text{SO}_4$ <sup>19</sup> can aid in the suppression of  $\text{H}_2\text{O}_2$  decomposition thus improving catalytic selectivity. Indeed it has recently been shown by Hutchings and co-workers<sup>8</sup> that it is possible to 'switch off' the hydrogenation and decomposition activity of a carbon supported bimetallic catalyst *via* an acid pre-treatment of the support. This has been shown to increase gold dispersion by producing smaller Au-Pd nanoparticles which are believed to be able to block the catalytic sites responsible for  $\text{H}_2\text{O}_2$  hydrogenation / decomposition. Further work by Hutchings and co-workers has shown that this acidic pre-treatment can also inhibit the degradation of  $\text{H}_2\text{O}_2$  by Au-Pd catalysts supported on  $\text{TiO}_2$ <sup>20</sup> and  $\text{SiO}_2$ <sup>9</sup>, however

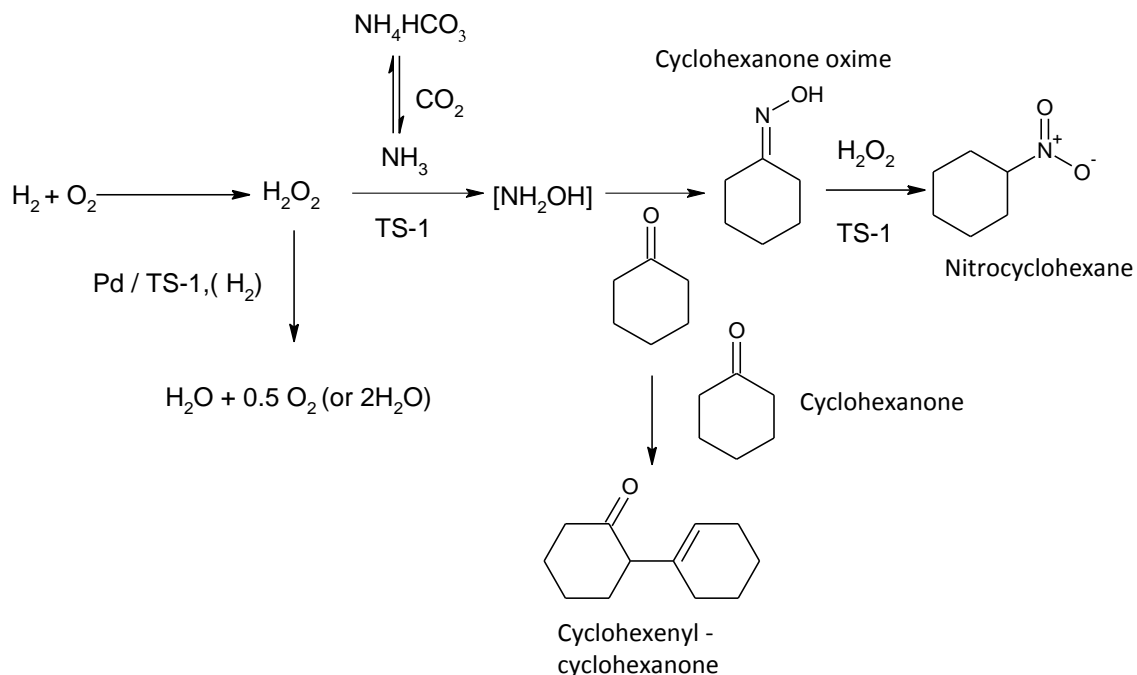
the pre-treatment is unable to completely inhibit  $\text{H}_2\text{O}_2$  degradation as seen when utilising a carbon support.

It is this work which has led to the investigation of highly acidic supports as a means by which catalyst selectivity towards  $\text{H}_2\text{O}_2$  may be improved. Sun and co-workers<sup>21</sup> have shown that Pd based heteropolyacid (HPA) catalysts offer both greater rates of  $\text{H}_2\text{O}_2$  synthesis, as well as improved selectivity towards  $\text{H}_2\text{O}_2$  synthesis in comparison to Pd catalysts utilizing more conventional supports. This work has led Hutchings and co-workers to investigate bi-metallic Au-Pd exchanged heteropolyacids in the direct synthesis of  $\text{H}_2\text{O}_2$ <sup>22,23</sup>.

The first part of the work reported herein attempts to build further on these earlier studies. However, instead of utilising Cs-exchanged HPAs as a support for metals known to be active towards  $\text{H}_2\text{O}_2$  synthesis, as studied previously within the Hutchings' group, their ability to promote catalyst activity towards  $\text{H}_2\text{O}_2$  synthesis is investigated when they are utilised as an additive in addition to a well-established  $\text{H}_2\text{O}_2$  synthesis catalyst.

The second part of this work is concerned with the formation of  $\text{H}_2\text{O}_2$  under the relatively challenging conditions associated with the ammoximation of cyclohexanone, that is the presence of elevated temperatures and basic conditions. The *in-situ* generation of  $\text{H}_2\text{O}_2$  during the ammoximation of cyclohexanone to cyclohexanone oxime would yield significant reductions in overall costs of the ammoximation reaction. Primarily these costs are associated with the purchasing, transport, storage and dilution of  $\text{H}_2\text{O}_2$ .

A suggested reaction scheme for the ammoximation of cyclohexanone is shown below, in Figure 1.2. It is observed that there are a number of competing, unwanted, side reactions that may contribute towards a decrease in the overall yield of cyclohexanone oxime. The role of catalyst design and reaction process optimization has been investigated in an attempt to improve the yield of cyclohexanone oxime.



**Figure 1.2.** Proposed reaction scheme for the ammoxidation of cyclohexanone via the in-situ synthesis of  $\text{H}_2\text{O}_2$ .

## 1.2. Catalysis, basic concepts and definitions.

Perhaps one of the most important industrial chemical reactions is the Haber-Bosch process, which leads to the production of artificial fertilisers and allows for the mass production of food. Without this process it is difficult to imagine how different the modern world would be. However the Haber-Bosch process is only one of a vast list of chemical processes that relies on the use of catalysis.

A large proportion of these catalysed reactions utilise a heterogeneous catalyst, where the catalyst itself is in a different phase to the reactants, often a solid catalyst with reactants in the liquid or gaseous phase. In comparison a homogenous catalyst exists in the same phase as the reactants, typically both catalyst and reactant will be gaseous or in the liquid phase.

It is possible to define a catalyst as a material that increases the rate of a chemical reaction by reducing the activation energy of a reaction ( $E_A$ ), but which is left unaltered at the end of the reaction. The lowering of the activation energy is achieved by the catalyst providing an alternative reaction pathway for the reaction to proceed, possibly through several intermediates or transition states, as seen in Figure 1.3. It can be seen that the activation barrier of the catalysed pathway is significantly lower than that on the un-catalysed route.

However, the Gibbs free energy of the system (G) is the same regardless of whether the reaction occurs in the presence of a catalyst or not. The Gibbs free energy may be defined in terms of enthalpy (H) and entropy (S) as the thermodynamic function of a system that is equal to the enthalpy minus the product of the absolute temperature (T) and entropy and an exact definition of G is therefore given by:

$$5. \quad G = H - TS$$

The Gibbs free energy is a measure of the tendency for a reaction to take place (a criterion of spontaneous change) as well as a measure of the useful work of a process. That is it combines two state functions and so it must be a state function itself. This means that the value of Gibbs free energy is dependent only on the initial and final state of the system. As such the presence of a catalyst will not alter the value of Gibbs free energy as a catalyst only provides a different pathway, of lower activation energy, for the reaction to proceed and does not alter the initial or final states of the system.

When a chemical reaction occurs the system is attempting to satisfy two opposing tendencies:

- 1) Towards maximum energy (maximum stability) and
- 2) Towards maximum entropy (maximum freedom).

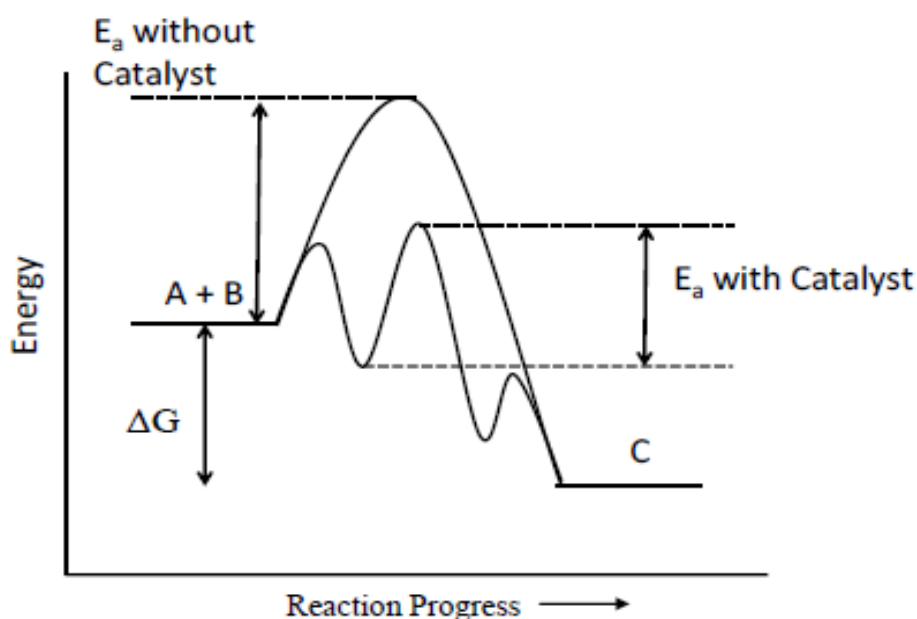
Therefore the change in Gibbs free energy ( $\Delta G$ ) is a measure of the tendency of a reaction to proceed and can be defined as:

$$6. \quad \Delta G = \Delta H - T\Delta S$$

The magnitude and sign of  $\Delta G$  provides information to how a reaction will proceed, with a large, negative value meaning that the reaction proceeds from reactants to products spontaneously. That is if a reaction results in a lowering of free energy it will be spontaneous. However, this means that it is possible that the reaction can occur not that it is certain to occur. Often a reaction may be highly favorable thermodynamically but occurs very slowly. It is kinetically unfavorable, as it has a high activation energy. The utilization of a catalyst will therefore affect the kinetics of the reaction.

At low reaction temperatures, the  $T\Delta S$  term will be relatively small in comparison to  $\Delta H$  so that  $\Delta G$  is insensitive towards the sign of the entropy change. The sign of  $\Delta G$  is therefore determined by the sign of  $\Delta H$ . At low temperatures the entropic contribution can be negative or positive but the Gibbs free energy change will be negative. Therefore, for a spontaneous

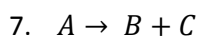
reaction  $\Delta H$  must be negative. However at high temperatures the  $(-T \Delta S)$  term will be dominant so that a positive  $\Delta S$  is needed for Gibbs free energy to be negative<sup>24</sup>.



**Figure 1.3.** Energy level diagram to compare the difference in the activation energy of a catalysed and non-catalysed reaction.<sup>24</sup>

Heterogeneous catalysts have a distinct advantage over homogeneous catalysts, mainly the ease in which they can be recovered and re-used. They provide a means for reactants to be brought together, on the active site of the catalyst, in such a way that reaction to the desired products are possible. It is therefore possible to correlate catalytic activity and the total number of active sites, in turn a high active surface area is often key in producing a highly active catalyst. The activity of a catalyst may be defined as the rate of reactant consumption (units: moles / dm<sup>3</sup>/s), although the activity to a particular product may also be quantified.

For a general reaction:



Catalytic activity towards A, B and C may be defined as:

$$8. \quad \text{Activity towards A} = (-d[A])/dt$$

$$9. \quad \text{Activity towards B} = (d[B])/dt$$

$$10. \quad \text{Activity towards C} = (d[C])/dt$$

A further term, known as specific activity can also be defined as:

$$11. A_{Sv} = \frac{-1}{S_v} * \frac{d[A]}{dt}$$

Where:

$S_v$  = total number of active sites per unit volume.

The specific activity is often very important for industrial application of catalysts, where the reactors used have a fixed volume for a catalyst to fill. Specific activity may also be expressed per unit weight of catalyst. Instead of expression in terms of unit volume it is possible to express specific activity per unit surface area, as shown in Equation 12.

$$12. A_{SV} = \frac{1}{b * S_A} * \frac{d[B]}{dt}$$

Where:

$b$  = the stoichiometric number of the conversion of one mole of reactant A to product B.

$S_A$  = the number of active sites per unit area of catalyst surface.

Finally an alternative expression, the turnover frequency (TOF), gives the rate in terms of molecules of A reacted per site per unit of time (usually seconds).

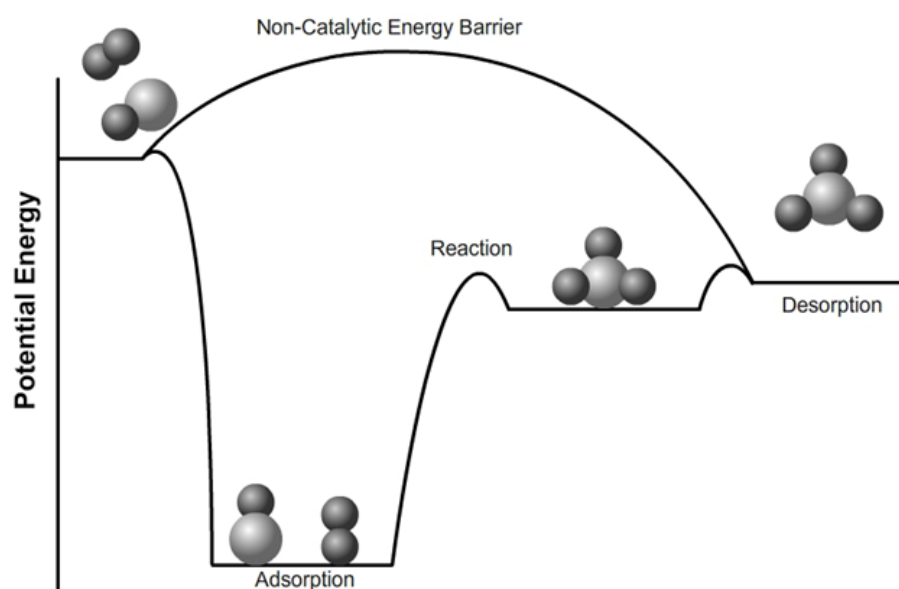
$$13. TOF = A_{SV} * N_A$$

Where  $N_A$  is Avagadro's number

To quantify the number of active sites ( $S_A$ ) it is first important to determine the total surface area of the catalytic metals on the surface of the support. This may be done through a process known as selective gas chemisorption, which is discussed in Chapter 2.

Often catalytic activity is improved through the dispersion of metal nanoparticles, often on an inert support. Typically metal oxides are utilised as they provide important physical features, such as high melting and decomposition temperatures, the ability to maintain a specific surface area when exposed to high temperatures, particularly when metal nanoparticles are affixed to them via thermal treatment. Furthermore other features such as pore volume and pore distribution can be established and provide significant benefit to the catalyst. With many reactions that utilise catalysts both the properties of the active phase and the support bring about the functionality of the catalyst.

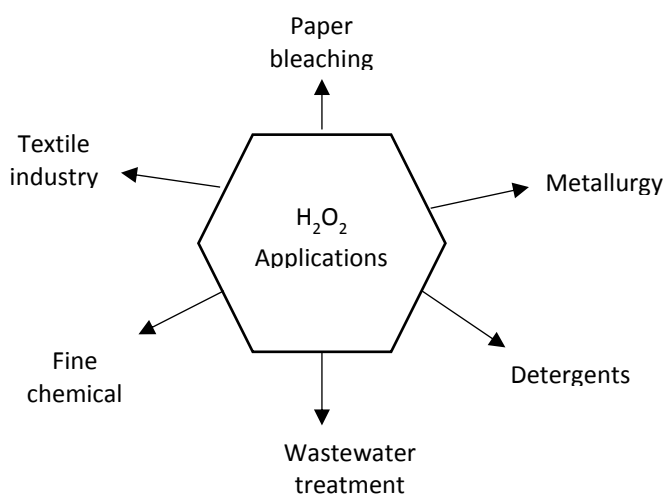
A general description of a catalytic process can be broken down into a number of basic steps; reactant adsorption onto the active site of the catalyst, breaking of the reactant bonds, reaction to form the products and the subsequent desorption of the newly formed products. These various steps are shown in Figure 1.4.



**Figure 1.4.** A basic energy diagram to show the potential steps that occur in a catalysed reaction<sup>25</sup>.

### 1.3. Introduction to hydrogen peroxide.

Hydrogen peroxide is a powerful, environmentally friendly, oxidant that is able to oxidise both inorganic and organic substrates, under mild conditions, and has a number of applications, summarized in Figure 1.5.<sup>26</sup>



**Figure 1.5.** Applications of  $\text{H}_2\text{O}_2$ <sup>26</sup>.

The global production of  $\text{H}_2\text{O}_2$  is estimated to exceed 2.2 million tons per annum and demand is believed to be growing at a rate of approximately 4 % per annum<sup>27</sup>. The principal industries that utilise  $\text{H}_2\text{O}_2$  are the pulp / paper bleaching and textile industries as well as water treatment where it is increasingly superseding chlorine containing oxidants<sup>11</sup>. In particular it is known that  $\text{H}_2\text{O}_2$  is able to destroy toxic chemicals present in industrial waste water such as thiocyanate, nitrate and hypochlorite. Furthermore  $\text{H}_2\text{O}_2$  finds use in mining, in particular in the extraction of gold and uranium<sup>11</sup>.

$\text{H}_2\text{O}_2$  has also been used in many application in the chemical sector, where it is used either directly or indirectly in the production of both organic and inorganic chemicals, such as hydrazine, ferric sulphate, iodic acid and perborates<sup>26</sup>, while typical uses of  $\text{H}_2\text{O}_2$  in organic synthesis include epoxidation<sup>28</sup>, hydroxylation<sup>29</sup> and oxidation<sup>29</sup>.

Furthermore  $\text{H}_2\text{O}_2$  is considered a reasonably safe chemical when handled in the correct manner and has the additional benefit of being soluble in water as well as a range of organic solvents. Hydrogen peroxides green credentials are well founded since the only by product of its oxidations is water and this, coupled with its nature as a highly effective oxidant, due to its high active oxygen content, has been a contributing factor in the growth in demand for  $\text{H}_2\text{O}_2$ . Indeed  $\text{H}_2\text{O}_2$  has been reported to be the best single-oxygen donor, next to molecular oxygen<sup>26</sup>. Owing to its low molecular weight  $\text{H}_2\text{O}_2$  is a more efficient oxidizing agent than other oxidants, such as sodium hypochlorite. Table 1.1 shows the efficiency of common industrially utilized oxidizing agents.

**Table 1.1.** The oxidizing efficiency of common industrial oxidants.

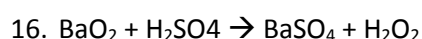
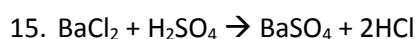
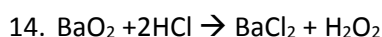
Oxidant	Active oxygen (% w/w)	By-product
$\text{H}_2\text{O}_2$	47.1	$\text{H}_2\text{O}$
$^t\text{BuOOH}$	17.8	$^t\text{BuOH}$
$\text{HNO}_3$	25.0	$\text{NO}_x$ , $\text{N}_2\text{O}$ , $\text{N}_2$
$\text{NaClO}$	21.6	$\text{NaCl}$
$\text{NaBrO}$	13.4	$\text{NaBr}$

#### 1.4. Historical note and current synthesis method.

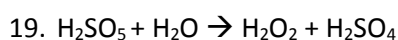
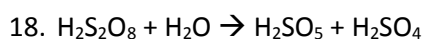
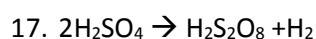
The manufacture of hydrogen peroxide can be traced back to its isolation by L .J. Thenard<sup>30</sup> in 1818, who reacted barium peroxide with nitric acid to give rise to a low concentration of aqueous hydrogen peroxide. It was discovered that this process can be improved greatly through the use of hydrochloric acid. The hydrogen peroxide is formed in combination with



barium chloride, which is removed by precipitation with sulphuric acid, shown in Equation 14. Thernard's process however had some major drawbacks; firstly only three per cent aqueous hydrogen peroxide solutions were produced using the barium peroxide based process and this led to high production costs and thus limited the market availability. Also the high level of impurities caused the stability of H<sub>2</sub>O<sub>2</sub> to be very poor. Thernard's route to H<sub>2</sub>O<sub>2</sub> is shown in Equations 14-16.



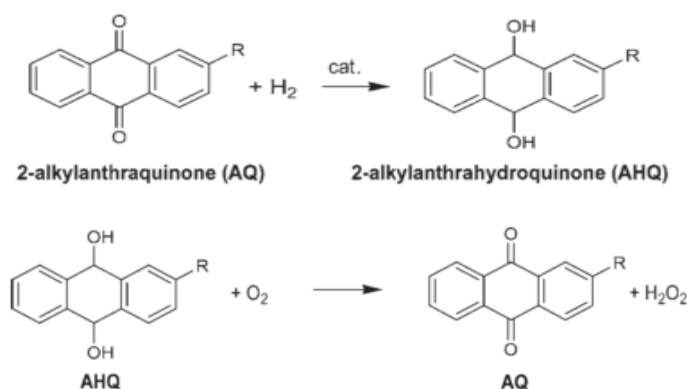
These difficulties were mostly alleviated when Meidinger discovered in 1853 that hydrogen peroxide could be formed electrolytically from sulphuric acid<sup>31</sup>. The electrochemical production process of aqueous H<sub>2</sub>O<sub>2</sub> is seen in Equations 17 - 19.



In 1901 Machot observed that autoxidizable compounds, such as hydroquinones react under alkaline conditions to form peroxides<sup>32</sup>. Subsequent to the work of Walton and Filson, who proposed the formation of H<sub>2</sub>O<sub>2</sub> via alternating oxidation and reduction of hydrazobenzene, Pfeleiderer developed a process for the alkaline autoxidation of hydrazobenzenes to produce sodium peroxide. In the Pfeleiderer approach sodium amalgam was utilised to reduce the azobenzene<sup>32</sup>.

Based on the work of Pfeleiderer<sup>1</sup> BASF developed the indirect anthraquinone process (AO process) in between 1939 and 1945, seen in Figure 1.6. This follows a route which involves the hydrogenation of a substituted anthraquinone, dissolved in a suitable solvent mixture at temperatures between 40-50 °C and under a partial pressure of hydrogen of no more than 4 bar. Carrier solutions are used, such as 2-tert-amylanthraquinone and 2-ethylanthraquinone, to yield a 'working' solution. The features of the AO process can be described as follows. A 2-alkylanthraquinone is dissolved in a suitable solvent and is catalytically hydrogenated to the corresponding 2-alkylanthrahydroquinone. The working

solution, containing 2-alkylanthrahydroquinone is then separated from the hydrogenation catalyst, usually palladium or nickel<sup>31</sup>. This is followed by aeration to reform the alkylanthraquinone and also produce hydrogen peroxide; demineralised water is then used to obtain H<sub>2</sub>O<sub>2</sub> in a counter current column. The hydrogen peroxide produced is approximately 30 % by weight and distillation techniques are employed to concentrate this to 70 % by weight and also remove impurities<sup>31</sup>.



**Figure 1.6.** The basic reaction scheme of the anthraquinone oxidation process.

The hydrogenation step in the original reduction of alkylanthraquinone employed a Raney nickel based catalysts. However, there were a number of drawbacks associated with this including limited selectivity, rapid deactivation and the pyrophoric nature of Raney nickel. A new generation of amorphous Ni / B<sup>33</sup> and Ni /Cr /B catalysts have been developed, which have proved to show selective carbonyl hydrogenation; hydrogenation of the aromatic rings of alkylanthraquinone is blocked. This is believed to be due to the ability of amorphous alloys to bond tightly with hydrogen.<sup>15</sup> It has been shown that Cr(III) promotes the hydrogenation of carbonyl groups by accepting the lone pair of the oxygen<sup>34</sup>. This activation favours attack of the carbon of the carbonyl group by dissociated hydrogen, adsorbed on to the nickel catalyst and causes greater selectivity of alkylanthraquinone in comparison to the alkylanthrahydroquinone. The most common catalysts employed in the hydrogenation of alkylanthraquinone are based on palladium, usually supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and Al<sub>2</sub>SO<sub>3</sub> / SiO<sub>2</sub><sup>26</sup>.

The indirect synthesis of hydrogen peroxide has been established on an industrial scale for many decades and as a result has become relatively efficient. However, a number of problems still exist. Firstly there is the inherent risk of using an oxygen-hydrogen gaseous mixture, under high pressure. The flammability limits of hydrogen in oxygen are between 4

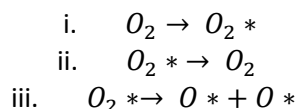
and 94 %<sup>11</sup> and therefore it is prudent to use concentrations of hydrogen below 4%, however this can result in decreased hydrogen peroxide yields. The fact that the anthraquinone process is only economically viable for large scale production means that the production of hydrogen peroxide occurs at a particular site, often some distance from where it will be utilised, followed by its transportation. The transport of highly concentrated hydrogen peroxide has associated safety concerns since  $\text{H}_2\text{O}_2$  can be explosive if allowed to decompose. Furthermore the catalytic reduction of the 2-alkylhydroanthraquinone dictates the need for continual replacement of the 2-alkylanthraquinone, this coupled with the need for continual regeneration of the catalyst represents two significant drawbacks to the AO process.

Even though the anthraquinone process has been made highly efficient its limitations have meant that other routes to the production of hydrogen peroxide are being investigated. This includes the use of photocatalysis<sup>35</sup>, electrolysis and the direct synthesis route, which strives to produce hydrogen peroxide from hydrogen and oxygen in a 'greener', one hundred per cent atom efficient route, which utilises a less expensive and less toxic solvent system.

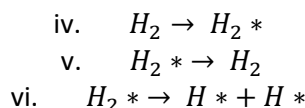
## 1.5. The proposed mechanism in the direct synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub>

It has generally been assumed that the formation of H<sub>2</sub>O<sub>2</sub> takes place via a two-step hydrogenation mechanism<sup>36-39</sup>, where a number of side reactions are involved. Possible elementary steps in the formation of H<sub>2</sub>O<sub>2</sub> and the competing side reactions are listed below.

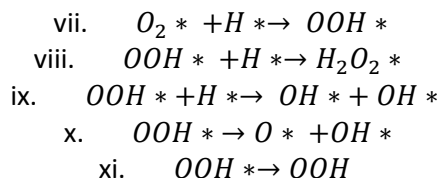
For the reactant O<sub>2</sub>:



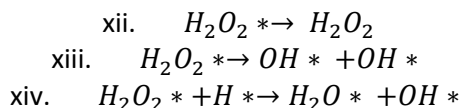
For the reactant H<sub>2</sub>



For the intermediate OOH:



For the product H<sub>2</sub>O<sub>2</sub>:



Where the asterisks (\*) represents the surface species on the metal catalyst, the hydrogenation steps vii and viii constitute the main reaction steps for the direct synthesis of H<sub>2</sub>O<sub>2</sub>. Steps ii, v and xi are the desorption of O<sub>2</sub>, H<sub>2</sub> and OOH respectively; and steps iii, vi, xi and xii are the dissociation of O<sub>2</sub>, H<sub>2</sub>, OOH or H<sub>2</sub>O<sub>2</sub>. The hydrogenation of OOH in step ix as well as the cleavage of the O-O bond present in the OOH species in step x hydrogenation of OOH leads to the cleavage of the O-O bond and as a result the formation of OH (hydroxyl species), subsequent hydrogenation of the OH species will then result in the formation of

water. Step xiv is the hydrogenation of  $\text{H}_2\text{O}_2$  to water and an OH group. All these side reactions involve the cleavage of the O-O bond and result in the formation of  $\text{H}_2\text{O}$ .

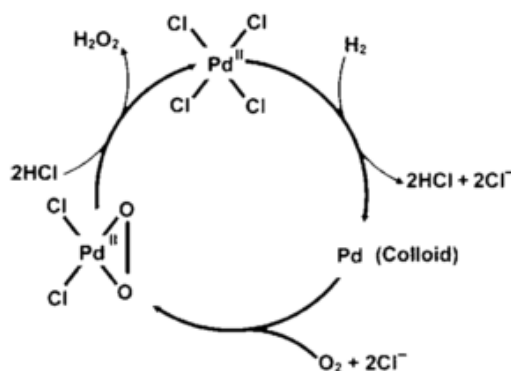
The comprehensive review by Yoshizawa and Li<sup>40</sup> reported the improved selectivity observed for a Au-Pd catalyst in comparison to a mono-metallic Pd only catalyst. Several extremely interesting findings are reported. Firstly, it is suggested that  $\text{H}_2$  adsorption and dissociation occurs at the Pd sites, as  $\text{H}_2$  dissociation is very facile and almost without an activation barrier. Secondly, on a Au-Pd bimetallic surface  $\text{O}_2$  will be located on a top-bridge-top position over one Au and one Pd atom. The formation of  $\text{H}_2\text{O}_2$  and undesired side reactions can be considered to be a competition between the formation of the O-O bond and the O-M bond (where M is Pd or Au). The O-Pd bond is calculated to be stronger than the O-O bond in the OOH and  $\text{H}_2\text{O}_2$  species, while the O-Au bond is much weaker, as a result the Au-Pd bimetallic surface shows improved selectivity towards  $\text{H}_2\text{O}_2$  than a pure Pd surface. However, it should be noted that this is based on the assumption that the more active Pd sites are occupied by dissociated H atoms. The need to maintain the O-O bond is considered key in the formation of  $\text{H}_2\text{O}_2$ . Lunsford has reported through isotopic labelling that the O-O bond is indeed maintained in the formation of  $\text{H}_2\text{O}_2$ , while O-O bond cleavage results in the formation of  $\text{H}_2\text{O}$ .

## **1.6. The palladium based catalyst in the synthesis of hydrogen peroxide.**

The direct synthesis of  $\text{H}_2\text{O}_2$  has long since been a research objective, with the very first patent being filed in 1914 by Henkel and Weber<sup>2</sup> and until quite recently the investigation of catalysts that may be appropriate for the direct synthesis of hydrogen peroxide have been solely based on palladium. However these earlier investigations utilised  $\text{H}_2$  /  $\text{O}_2$  mixtures within the explosive range, which has obvious associated dangers, which would be magnified greatly for any commercial operation.

The work of Lunsford<sup>4,6,41</sup> has shown that palladium supported catalysts show high activity towards the direct formation of hydrogen peroxide, however as with previous studies involving palladium only catalysts the presence of halides is required in order for the catalyst to show high selectivity. Further work by Lunsford<sup>5,42</sup> has indicated that the high activity of palladium catalysts can be attributed to the formation of colloidal palladium, particularly

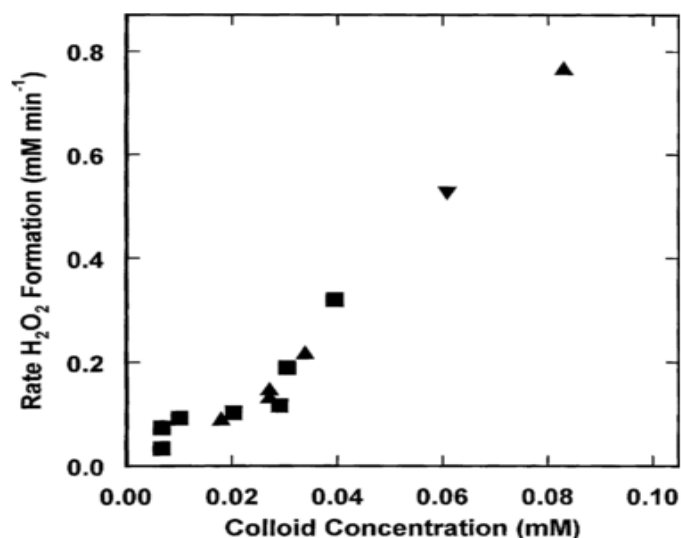
when  $\text{PdCl}_2$  and  $\text{Pd} / \text{SiO}_2$  were used as the catalyst. Figure 1.7 shows the formation of colloidal palladium from  $\text{Pd} / \text{SiO}_2$  catalyst during the direct synthesis process and the catalytic cycle thought to be responsible for the production of hydrogen peroxide<sup>43</sup>.



**Figure 1.7.** The formation of colloidal palladium from a Palladium tetrachloride species<sup>43</sup>.

In the presence of hydrochloric acid supported metallic palladium has been shown to be initially oxidised to  $\text{PdCl}_4^{2-}$  ions, these ions are reduced back to metallic palladium by hydrogen, where some of the palladium that is not reduced being present in the colloidal form<sup>43</sup>. The role of palladium colloids in the catalytic formation of hydrogen peroxide has arisen from two main observations. The first is that the rate of hydrogen peroxide formation did not change after the  $\text{Pd} / \text{SiO}_2$  catalyst was removed and secondly faster rates were observed when no support was present, when palladium chloride was utilised as the catalyst<sup>44</sup>.

Additionally Lunsford<sup>44</sup> has shown that the rate of  $\text{H}_2\text{O}_2$  formation is 'approximately proportional' to the concentration of colloidal palladium, as seen in Figure 1.8. Dissanayke and Lunsford<sup>44</sup> reported that colloidal palladium is an active phase for the formation of  $\text{H}_2\text{O}_2$  from  $\text{H}_2$  and  $\text{O}_2$  in an  $\text{HCl}$  acidified aqueous medium. As eluded to above the rate of  $\text{H}_2\text{O}_2$  formation is almost constant for 3-5 hours but after this period the rate of formation and the concentration of  $\text{H}_2\text{O}_2$  began to decrease. It is appropriate, therefore to consider colloidal palladium as a homogeneous catalyst for the direct synthesis of  $\text{H}_2\text{O}_2$ . This work by Dissanayke and Lunsford<sup>44</sup> and subsequent work by Chinta and Lusford<sup>43</sup> has suggested that the presence of  $\text{HCl}$  and  $\text{O}_2$  facilitated the dissolution of Palladium from  $\text{Pd} / \text{SiO}_2$  catalysts.



Variation in catalytic activity for H<sub>2</sub>O<sub>2</sub> formation as a function of colloid concentration with the colloid being derived from: ■, 10<sup>-3</sup> M PdCl<sub>2</sub>; ▲, 5 wt% Pd/SiO<sub>2</sub>(57); ▼, 5 wt% Pd/SiO<sub>2</sub>(03).

**Figure 1.8.** The dependence of hydrogen peroxide rate of formation of colloidal Palladium concentration<sup>44</sup>.

Although colloidal palladium is extremely interesting at a research level it is accepted that it is not suitable for commercial use as the management of the colloid is a difficult task. One of the major drawbacks of colloidal Pd is the short lifetime of the catalyst and a number of attempts to stabilize colloidal Pd, through the use of sodium citrate, poly(vinyl alcohol) and poly(ethylene glycol) have proved to be unsuccessful<sup>44</sup>. In particular the use of PVP stabilized colloidal Pd has shown promise as a catalyst for the Heck coupling reaction<sup>45</sup>.

Choudhary and co-workers<sup>3,46,47</sup> have also studied palladium based catalysts for the direct synthesis of hydrogen peroxide and they and others have shown that the decomposition of hydrogen peroxide over supported palladium catalysts strongly depends on the oxidation state of the palladium. Supported PdO / C catalysts have been shown to have a much greater selectivity and much lower activity for hydrogen peroxide decomposition (approximately 70 %) than the corresponding Pd<sup>0</sup> / C catalysts, with decomposition reported to be near 100 % in water<sup>47,48</sup>. The tendency for H<sub>2</sub>O<sub>2</sub> to adsorb onto the Pd<sup>0</sup> surface rather than that of PdO has been suggested as the reason for the higher selectivity observed for the PdO catalyst<sup>49</sup>.

It is possible to alter the hydrogen peroxide decomposition activity of the Pd<sup>0</sup> catalysts via oxidative heat treatment, with the formation of PdO it is possible to a more selective catalyst through inhibition of the H<sub>2</sub>O<sub>2</sub> decomposition pathway. Often the surface reduction of PdO to Pd<sup>0</sup> due to the presence of H<sub>2</sub> in the reaction solvent has been attributed as the reason for

the increase in hydrogen peroxide decomposition for these catalysts, even in the presence of protons in the aqueous media, it is the ability of  $\text{Pd}^0$  to form Pd-H intermediate species which is suggested to assist in the decomposition of hydrogen peroxide<sup>50</sup>.

Choudhary *et.al.*<sup>50</sup> have claimed that a PdO catalyst is better suited to be used in hydrogen peroxide synthesis, many others including Lunsford and Chinta<sup>43</sup>, and Burch and Ellis<sup>51</sup> have claimed that higher hydrogen peroxide productivity and selectivity can be achieved with  $\text{Pd}^0$  catalysts. As PdO is typically reduced in the presence of  $\text{H}_2$  it may be expected that, under reaction conditions a mixed oxidation state prevails, with both  $\text{Pd}^0$  and  $\text{Pd}^{2+}$  present, with both reduced and oxidized Pd providing different selectivity and activity towards  $\text{H}_2\text{O}_2$ . It is suggested that the ratio of these two Pd species is key in producing an active catalyst that is also selective towards  $\text{H}_2\text{O}_2$ .

Hutchings and co-workers have studied palladium catalysts on a variety of supports ( $\text{Al}_2\text{O}_3$ <sup>12</sup>,  $\text{SiO}_2$ <sup>9</sup>,  $\text{TiO}_2$ <sup>15</sup>,  $\text{Fe}_2\text{O}_3$ <sup>13</sup>,  $\text{MgO}$ <sup>52</sup>, carbon<sup>53</sup>) and these findings are summarised in Table 1.2. The decomposition and hydrogenation of  $\text{H}_2\text{O}_2$  have been decoupled and are reported separately. The rate of catalytic decomposition is determined by utilising a known concentration of  $\text{H}_2\text{O}_2$  (approximately 4 wt %) and a 25 %  $\text{O}_2$  /  $\text{CO}_2$  atmosphere, this prevents the hydrogenation reaction from occurring. By determination of the concentration of  $\text{H}_2\text{O}_2$  post reaction it is possible to calculate the activity towards  $\text{H}_2\text{O}_2$  decomposition. By then investigating the total degradation of  $\text{H}_2\text{O}_2$  (in a similar manner to that described for  $\text{H}_2\text{O}_2$  decomposition) through the use of a 5 %  $\text{H}_2$  /  $\text{CO}_2$  atmosphere it is possible to separate the individual degradation pathways. The carbon supported Pd catalyst was found to be the most effective, providing the greatest productivity ( $55 \text{ mol}_{\text{H}_2\text{O}_2} \text{Kg}_{\text{cat}}^{-1} \text{h}^{-1}$ ) and lowest rate of hydrogenation ( $135 \text{ mol}_{\text{H}_2\text{O}_2} \text{Kg}_{\text{cat}}^{-1} \text{h}^{-1}$ ) as well as a comparatively low rate of decomposition ( $118 \text{ mol}_{\text{H}_2\text{O}_2} \text{Kg}_{\text{cat}}^{-1} \text{h}^{-1}$ ). It is suggested by the authors that the catalytic selectivity is related to the isoelectric point of the supports, with the isoelectric point reported to follow the trend  $\text{C} > \text{TiO}_2 > \text{Al}_2\text{O}_3 > \text{MgO}$ . The relationship between isoelectric point of the support and the degradation of  $\text{H}_2\text{O}_2$  generally holds with the MgO supported catalyst reported to have the greatest rates of  $\text{H}_2\text{O}_2$  decomposition and hydrogenation and the greatest isoelectric point. It would be of interest to determine the stability of the MgO. The formation of  $\text{Mg}(\text{OH})_2$  may explain the greater rates of  $\text{H}_2\text{O}_2$  degradation observed for Pd / MgO catalyst as<sup>55</sup> it is known that  $\text{H}_2\text{O}_2$  is highly unstable under basic conditions<sup>11</sup>.



**Table 1.2.** The efficiency of supported palladium catalysts in the direct synthesis of hydrogen peroxide.

Catalyst	H <sub>2</sub> O <sub>2</sub> hydrogenation / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> Kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> <sup>a</sup>	H <sub>2</sub> O <sub>2</sub> decomposition / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> Kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> <sup>b</sup>	H <sub>2</sub> O <sub>2</sub> productivity / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> Kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> <sup>c</sup>	H <sub>2</sub> Selectivity / % <sup>d</sup>
Pd/Al <sub>2</sub> O <sub>3</sub> <sup>12</sup>	200	24	9	<i>n.d</i>
Pd/TiO <sub>2</sub> <sup>15</sup>	288	247	30	21
Pd/MgO <sup>54</sup>	582	405	29	<i>n.d</i>
Pd/C <sup>54</sup>	135	118	55	34

**Reaction conditions:** **a** Rate of hydrogenation of H<sub>2</sub>O<sub>2</sub> calculated from amount of H<sub>2</sub>O<sub>2</sub> hydrogenated using standard reaction conditions: 2.9 MPa 5 % H<sub>2</sub> / CO<sub>2</sub>, 8.5 g solvent (5.6 g MeOH, 2.22 g H<sub>2</sub>O and 0.68 g 50 wt. % H<sub>2</sub>O<sub>2</sub>), 0.01 g catalyst, 2 °C, 1200 rpm, 30 min.

**b** Rate of decomposition of H<sub>2</sub>O<sub>2</sub> calculated from H<sub>2</sub>O<sub>2</sub> decomposed using standard reaction conditions: 2.9 MPa 25 % O<sub>2</sub> / CO<sub>2</sub>, 8.5 g solvent (5.6 g MeOH, 2.9 g H<sub>2</sub>O and 0.68 g 50 wt. % H<sub>2</sub>O<sub>2</sub>), 0.01 g catalyst, 2 °C, 1200 rpm.

**c** Rate of hydrogen peroxide production determined after reaction: 5 % H<sub>2</sub> / CO<sub>2</sub> and 25 % O<sub>2</sub> / CO<sub>2</sub>, 1 : 2 H<sub>2</sub> / O<sub>2</sub> at 3.7 MPa, 5.6g MeOH, 2.9 g H<sub>2</sub>O, 0.01 g catalyst and 1200 rpm).

**d** Hydrogen selectivity calculated by analysis of the reaction gases before and after reaction using the standard condition.

**n.d.** = not determined due to low reproducibility.

The dispersion of metal is often a critical aspect in a number of catalytic reactions, including the direct synthesis of H<sub>2</sub>O<sub>2</sub>. It has been observed by Menegazzo *et.al.*<sup>56</sup> that to produce an active, yet selective catalyst a compromise must be reached between high metal dispersion to increase catalytic activity and the presence of less energetic sites, where O<sub>2</sub> can adsorb without cleavage of the O-O bond. Further work by this group<sup>54</sup> has established that a Pd loading, on a SiO<sub>2</sub> support and under mild reaction conditions, of 1.5 wt. % is optimal for catalytic activity and selectivity. Furthermore they establish that the choice of support is key in controlling metal dispersion, with SiO<sub>2</sub> proven to be more efficient than a number of supports including CeO<sub>2</sub> and ZrO<sub>2</sub>. It is observed that the mean size of the Pd nanoparticles in the highly selective (approximately 60 %) and active catalyst 1.5 wt. % Pd / SiO<sub>2</sub> catalyst is 5 nm, while the use of CeO<sub>2</sub> or ZrO<sub>2</sub> as a support produces nanoparticles with a mean size of 1 nm. The 1.5 wt. % Pd / CeO<sub>2</sub> and 1.5 wt. % Pd / ZrO<sub>2</sub> catalysts are observed to be much less selective (approximately 45 % for both catalysts). The authors suggest that the presence of smaller (1 nm) Pd nanoparticles, containing more energetic sites are able to chemisorb and dissociate O<sub>2</sub>. The resultant atomic oxygen is then key in the formation of water and lowering of catalytic selectivity towards H<sub>2</sub>O<sub>2</sub>.

Further work by Abate and co-workers<sup>56</sup> was carried out investigating the effect of particle size on the direct synthesis of H<sub>2</sub>O<sub>2</sub>. Pd catalysts supported on ceramic asymmetric tubular alumina membranes were prepared by two distinct techniques (i) reduction with N<sub>2</sub>H<sub>4</sub> in an ultrasonic bath and (ii) by impregnation deposition resulted in two catalysts with distinct differences in mean particle diameter. The former technique produces metal nanoparticles

with an average particle diameter of 11 nm, while the latter technique produces metal nanoparticles with an average particle diameter of 4nm. Investigation into catalyst selectivity towards  $\text{H}_2\text{O}_2$  reveals that the samples with the larger Pd nanoparticles shows a higher pseudo-rate constant of direct synthesis of  $\text{H}_2\text{O}_2$  in comparison to catalysts comprising smaller metal nanoparticles. In addition it is reported that the catalyst comprising larger metal nanoparticles are observed to offer a  $\text{H}_2\text{O}_2$  combustion rate six times lower than the catalyst with a smaller average particle size.

Ouyang and co-workers<sup>57</sup> have investigated the role of Pd-PdO domains in the direct synthesis of  $\text{H}_2\text{O}_2$ , when utilising  $\text{TiO}_2$  as a support. They report that the composition of surface Pd is a significant factor in determining catalytic selectivity and activity. It is reported that both total metal loading and pre-treatment of the catalyst are key parameters in catalyst design and may be utilised to tune catalyst performance. By lowering total Pd loading from 5 wt. % to 1 wt. % it is possible to improve both selectivity towards  $\text{H}_2\text{O}_2$  (from 41 to 61 %) and  $\text{H}_2\text{O}_2$  productivity (from 1.24 to 2.99  $\text{mol}_{\text{H}_2\text{O}_2}\text{g}_{\text{Pd}}^{-1}\text{h}^{-1}$ ). Interestingly the size of Pd nanoparticles is reported to stay relatively constant, at approximately 2.5 nm regardless of total metal loading. This improvement in catalytic performance is ascribed partly to the ratio of Pd : PdO. As metal loading is lowered the concentration of PdO on the surface of the nanoparticles is reported to increase. The authors suggest that  $\text{O}_2$  preferentially adsorbs onto low co-ordination Pd sites and the presence of the Pd-PdO interface results in a weakening of the interaction between adsorbed  $\text{O}_2$  and Pd. This is considered beneficial for improving catalytic selectivity towards  $\text{H}_2\text{O}_2$ .

## **1.7. Gold based catalysts in the synthesis of hydrogen peroxide.**

The catalytic ability of gold has received an ever growing interest, its effectiveness as an oxidation<sup>58</sup> and hydrogenation<sup>59</sup> catalyst has found favour in various branches of chemistry. Its uses vary from low temperature oxidation of carbon monoxide<sup>58</sup> to hydrochlorination of acetylene<sup>62</sup> and the epoxidation of propylene<sup>61</sup>.

Hutchings and co-workers<sup>12</sup> were the first to show that Au catalysts were effective in the direct synthesis of  $\text{H}_2\text{O}_2$ , they provide high selectivity, but relatively low formation rates. When compared to their palladium analogues, using supercritical carbon dioxide as a reaction medium (35 °C, 9.7 MPa) it was found that gold was active in the formation of

hydrogen peroxide. Subsequent experiments, using a water / methanol solvent showed that at lower temperatures (2 °C) hydrogen peroxide synthesis occurs at a higher rate over Au / Al<sub>2</sub>O<sub>3</sub> in comparison to Pd / Al<sub>2</sub>O<sub>3</sub> supported catalysts<sup>62</sup>, with values of catalytic productivity reported as 1530 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> x10<sup>-3</sup> and 370 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> x10<sup>-3</sup> for the Au and Pd / Al<sub>2</sub>O<sub>3</sub> respectively. Subsequently Haruta and co-workers<sup>63</sup> have shown that Au/SiO<sub>2</sub> catalysts are effective for direct hydrogen peroxide synthesis. They concluded that catalyst activity was related to metal particle size, where calcination had increased Au particle size catalyst activity was found to have decreased. Ishihara<sup>42</sup> has also demonstrated that gold is an effective catalyst for hydrogen peroxide formation, although the catalyst activity depends on the support used.

In view of these findings Hutchings and co-workers have investigated gold on a range of supports at low temperature using a CH<sub>3</sub>OH / H<sub>2</sub>O solvent, including Al<sub>2</sub>O<sub>3</sub><sup>12</sup>, Fe<sub>2</sub>O<sub>3</sub><sup>13</sup>, SiO<sub>2</sub><sup>14</sup>, TiO<sub>2</sub><sup>15</sup>, carbon<sup>64</sup>, zeolite Y and ZSM-5<sup>65</sup>. In addition the use of Cs-exchanged tungstophosphoric acid has also been investigated as a support for Au<sup>66</sup>. Comparison of gold on these various supports, summarized in Table 1.3, has shown that these catalysts have very little activity towards the synthesis of H<sub>2</sub>O<sub>2</sub>, compared to their palladium analogues, under the reaction conditions used. Furthermore gold supported catalysts have been shown to have lower hydrogen peroxide degradation rates than the analogous Pd catalysts.

Comparison of supported mono-metallic Au and Pd catalysts is observed in Table 1.4. Interestingly the 5 wt. % Au / Cs<sub>2.8</sub>H<sub>0.2</sub>PW<sub>12</sub>O<sub>40</sub> catalysts offers lower H<sub>2</sub>O<sub>2</sub> hydrogenation rates than the bare support, with the rate of H<sub>2</sub>O<sub>2</sub> hydrogenation of the Cs<sub>2.8</sub>H<sub>0.2</sub>PW<sub>12</sub>O<sub>40</sub> support reported as 162 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> and that of the 5 wt. % Au / Cs<sub>2.8</sub>H<sub>0.2</sub>PW<sub>12</sub>O<sub>40</sub> catalyst reported as 103 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>. This suggests that the incorporation of Au onto the support blocks sites responsible for this reaction.

**Table 1.3.** The efficiency of supported Gold catalysts in the direct synthesis of hydrogen peroxide.

Catalyst	H <sub>2</sub> O <sub>2</sub> Hydrogenation / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> Kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	H <sub>2</sub> O <sub>2</sub> decomposition / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> Kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	H <sub>2</sub> O <sub>2</sub> productivity / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> Kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>
5 %Au/Al <sub>2</sub> O <sub>3</sub>	229	18	2.6
5% Au/ TiO <sub>2</sub> <sup>67</sup>	71	24	7
5% Au/MgO <sup>16</sup>	100	12	0
5% Au / C <sup>16</sup>	0	0	1
4.3 % Au / Zeolite Y <sup>66</sup>	<i>n.d.</i>	<i>n.d.</i>	2.99
4.3% Au / ZSM-5 <sup>68</sup>	<i>n.d.</i>	<i>n.d.</i>	1.75
5% Au / CS <sub>2.8</sub> H <sub>0.2</sub> PW <sub>12</sub> O <sub>40</sub> <sup>66</sup>	103	<i>n.d.</i>	14

**Reaction conditions:** As outlined in Table 1.2.**n.d.** = not determined.**Table 1.4.** Comparison of mono-metallic Au and Pd catalysts towards the direct synthesis and degradation of H<sub>2</sub>O<sub>2</sub>.

Catalyst	H <sub>2</sub> O <sub>2</sub> hydrogenation/ mol <sub>H<sub>2</sub>O<sub>2</sub></sub> Kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	H <sub>2</sub> O <sub>2</sub> decomposition /mol <sub>H<sub>2</sub>O<sub>2</sub></sub> Kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	H <sub>2</sub> O <sub>2</sub> productivity/ mol <sub>H<sub>2</sub>O<sub>2</sub></sub> Kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>
5 %Pd/TiO <sub>2</sub> <sup>67</sup>	288	247	30
5% Au / TiO <sub>2</sub> <sup>67</sup>	71	24	7
5% Pd / MgO <sup>16</sup>	582	405	29
5% Au / MgO <sup>16</sup>	100	12	0
5% Pd / C <sup>16</sup>	135	118	55
5 % Au / C <sup>16</sup>	0	0	1
5% Pd / CS <sub>2.8</sub> H <sub>0.2</sub> PW <sub>12</sub> O <sub>40</sub> <sup>66</sup>	281	<i>n.d.</i>	136
5% Au / CS <sub>2.8</sub> H <sub>0.2</sub> PW <sub>12</sub> O <sub>40</sub> <sup>66</sup>	103	<i>n.d.</i>	14

**Reaction Conditions:** As outlined in Table 1.2.**n.d.** = not determined.

Ishihara *et al.*<sup>69</sup> have studied various Au supported catalysts in the direct synthesis of hydrogen peroxide. It was concluded that the catalysts that offered the most promise were Au / SiO<sub>2</sub> and Au / Cu<sub>2</sub>O, with Au / SiO<sub>2</sub> exhibiting the smallest decomposition activity, and

the greatest activity towards hydrogen peroxide synthesis. These findings are at odds somewhat with those of Hutchings and co-workers<sup>15</sup> who have reported that TiO<sub>2</sub> is the most effective support for Au in the synthesis of hydrogen peroxide. However the reaction conditions of these studies were different and this may indicate the sensitivity of the reaction to the conditions in which it takes place.

### **1.8. Bimetallic catalysts for the direct synthesis of hydrogen peroxide.**

The observation that Au-Pd bimetallic catalysts showed greater hydrogen peroxide productivity than either monometallic catalysts was initially reported by Hutchings and co-workers<sup>15, 53, 70</sup> and subsequent work on Au-Pd on a range of supports has indicated that a synergistic effect is observed when both metals are combined on the same support. As noted by Hutchings and co-workers<sup>12, 13, 15</sup> supported Au-Pd (1:1 by wt. %) catalysts produced significantly more H<sub>2</sub>O<sub>2</sub> than the mono-metallic Au and Pd catalyst. With the surface ratio of Au : Pd reported to increase to 1 to 7 upon calcination, as determined by XPS<sup>71</sup>. This is associated with the development of Au-core PdO-shell nanoparticles

Further studies by Han *et.al*<sup>72</sup> have reported that there is an optimum Au- Pd composition (Au : Pd ~ 1.5 : 1) where rate of formation is much greater than for either the gold only or palladium only supported catalysts. In this study the rate of H<sub>2</sub>O<sub>2</sub> formation reaches a maxima at a Au : Pd ratio of 1.5 : 1 but then decreased by approximately 50 % as Au : Pd ratio increased to 3.4 : 1. However, selectivity towards H<sub>2</sub>O<sub>2</sub> increases slightly as the catalyst becomes more Au-rich; from 59 to 62 % as the Au : Pd ratio increases from 1.5 : 1 to 3.4 : 1. The authors suggest that both the modification of the electronic structure of Pd by Au as well as reconstruction of the surface composition, for example, by tuning the Pd-Pd bond length are responsible for the enhanced selectivity towards H<sub>2</sub>O<sub>2</sub>. For the first case, it is suggested that there is a transfer of electrons from the s and p orbitals of the Au to the Pd d orbitals and the resulting transfer of negative charge alters the catalytic properties of Pd. For example by suppression of O-O bond cleavage, known to lead to the formation of H<sub>2</sub>O. For the second case, there is a significant loss of surface Pd, resulting in an increase in selectivity towards H<sub>2</sub>O<sub>2</sub> by inhibition of the various H<sub>2</sub>O<sub>2</sub> degradation pathways.

Gudarzi *et.al*<sup>73</sup>. have investigated the promotive effect of Au in Au-Pd bimetallic catalysts supported on activated carbon cloth for activity towards the synthesis of H<sub>2</sub>O<sub>2</sub>. They report that by increasing Au : Pd ratio from 1 : 4 to 1 : 2 it was possible to improve selectivity towards H<sub>2</sub>O<sub>2</sub> from 47 % to 63 %. However catalytic activity toward H<sub>2</sub>O<sub>2</sub> drops significantly from 1025 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> for the Pd-rich catalyst to 514 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> for the Au-rich catalyst.

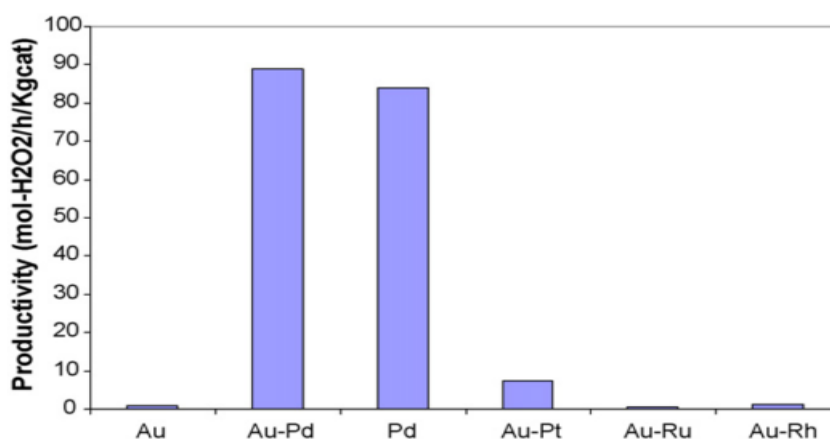
Interestingly it has been reported by Hutchings and co-workers<sup>12</sup> that Au-Pd supported catalyst are effective in the formation of hydrogen peroxide without the presence of acid and halide ions, in a water medium. This is due to the choice of reaction conditions, where CO<sub>2</sub> is utilized as the reaction gas diluent, initially in order to ensure that hydrogen is kept below its explosive limits but it has been discovered since that CO<sub>2</sub> acts as an in-situ acid promoter. It is suggested any commercial application of hydrogen peroxide is likely to favor a water medium in comparison to an organic one and so this is considered to be an important discovery in the development of bimetallic catalysts.

Choudhary and co-workers<sup>74</sup> have compared the effect that various noble metal additives have on supported palladium catalysts in the direct synthesis of hydrogen peroxide. It was reported that the addition of Au to Pd improved the conversion of hydrogen, from approximately 35 % (when no Au is present) to a maxima of 50 % when a Au : Pd ratio of 0.11 is investigated. As well as an improvement in H<sub>2</sub> conversion there is an increased rate of H<sub>2</sub>O<sub>2</sub> synthesis, however the optimal Au : Pd ratio for H<sub>2</sub>O<sub>2</sub> synthesis is observed to be approximately 0.02, beyond this ratio the yield of H<sub>2</sub>O<sub>2</sub> decreases.

The investigation also established that platinum may also be used as an additive in palladium catalysts, with increasing platinum content the yield of H<sub>2</sub>O<sub>2</sub> rose to a maxima of 15 % when a Pt : Pd ratio of approximately 0.02 was utilized. It is important to note that the initial increase in hydrogen peroxide yield was lower than that seen for the corresponding Au-Pd catalyst. In addition it is noteworthy to mention that hydrogen peroxide yield at higher platinum concentrations decreased below that of monometallic palladium catalysts and this was attributed to the increase in hydrogen peroxide decomposition activity and decreasing stability of the hydroperoxy precursor.<sup>51,74</sup> The authors suggest that the improvement observed when Au is used in addition to Pd is due to the ability of Au to form stable hydroperoxy (OOH) species, which is considered to be the precursor for H<sub>2</sub>O<sub>2</sub>. This decreased stability has been linked to greater ability of platinum to catalyse O-O bond breaking<sup>51</sup>.

Finally it was reported by Hutchings<sup>60</sup> that the incorporation of ruthenium and rhodium into palladium supported catalyst was detrimental to hydrogen peroxide yield. These Ru-Pd and Rh-Pd catalysts show an increase in hydrogen conversion with increasing metal content, however there is also a corresponding rise in hydrogen peroxide decomposition.

As can be seen in Figure 1.9 the addition of both Pt and Pd to Au improves productivity over the monometallic Au catalyst, while the incorporation of Ru or Rh into a Au catalyst does not improve catalytic productivity.



Performance of 2.5 wt.% metal/Y for the synthesis of H<sub>2</sub>O<sub>2</sub>, the 2.5 wt.% Au and Pd catalysts are also shown. Reaction condition: Methanol 5.6 g, water 2.9 g, catalyst 10 mg, 5% H<sub>2</sub>/CO<sub>2</sub> 420 psi, 25% O<sub>2</sub>/CO<sub>2</sub> 150 psi, temperature 2 °C, reaction time 0.5 h.

**Figure 1.9.** The effect of metal additives in the productivity of catalyst towards H<sub>2</sub>O<sub>2</sub>.<sup>60</sup>

Further comparison between Pd-Au and Pd-Pt catalysts supported on the macroreticular ion-exchange resin Lewatit K2621 has been conducted by Sterchele *et al.*<sup>75</sup>. It is reported that the addition of Au to Pd to produce a 0.25 wt. % Au – 1 wt. % Pd / K2621 catalyst improves catalytic selectivity towards H<sub>2</sub>O<sub>2</sub> from approximately 65 % for the 1 wt. % Pd / K2621 catalyst to approximately 75 % for the 0.25 wt. % Au – 1 wt. % Pd / K2621 catalyst. In comparison the addition of 0.25 wt % Pt to the 1 wt. % Pd / K2621 catalyst lowers catalytic selectivity towards H<sub>2</sub>O<sub>2</sub> to approximately 38 %. The authors suggest that the improvement in catalytic selectivity observed for the 0.25 wt. % Au – 1 wt. % Pd / K2621 catalyst is a result of increased average nanoparticle size. It is reported that average nanoparticle diameter increases from 4.6 nm for the 1 wt. % Pd / K2621 catalyst to 11 nm for the 0.25 wt. % Au – 1 wt. % Pd / K2621 catalyst, while the addition of Pt to Pd decreases average nanoparticle diameter to 3.3 nm for the 0.25 wt. % Pt - 1 wt. % Pd / K2621 catalyst. It is suggested that these smaller metal nanoparticles have greater activity for the cleavage of the O-O bond resulting in the

formation of  $\text{H}_2\text{O}$ . As such catalytic selectivity towards  $\text{H}_2\text{O}_2$  is greatest over the larger Au-Pd nanoparticles

Zhang and co-workers<sup>76</sup> have investigated Pd-Ag catalysts supported on activated carbon for the direct synthesis of  $\text{H}_2\text{O}_2$ , they demonstrate that the presence of Ag prevents the degradation of  $\text{H}_2\text{O}_2$  and improves catalytic selectivity through increasing the concentration of surface PdO. The enhanced selectivity of PdO over Pd has previously been demonstrated by Choudhary et.al.<sup>43</sup> and is discussed in Section 1.6. In addition Zhang and co-workers<sup>76</sup> ascribed the increase in selectivity to electronic interactions between Pd and Ag in addition to inhibition of  $\text{H}_2$  and  $\text{O}_2$  adsorption by coverage of the Pd surface by Ag. By optimizing the ratio of Pd : Ag it is possible to improve catalytic selectivity towards  $\text{H}_2\text{O}_2$  from 54 to 71 % for the monometallic Pd and the optimized Pd-Ag ( $\text{PdAg}_{40}$ , with Pd : Ag of approx. 40 : 1) supported catalyst respectively.

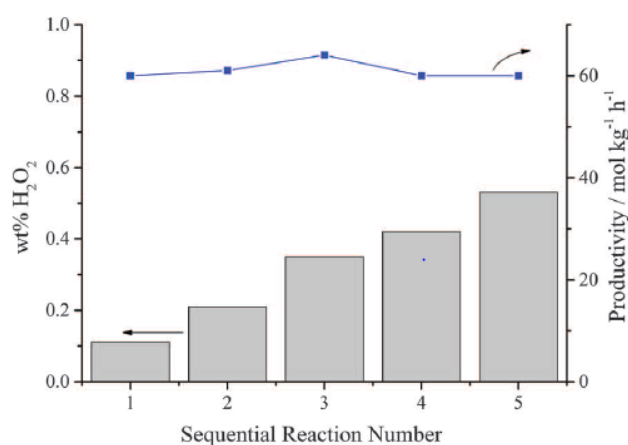
Gudarzi *et.al.*<sup>77</sup> have shown that the selectivity towards  $\text{H}_2\text{O}_2$  as well as  $\text{H}_2\text{O}_2$  yield of catalysts containing both Au and Pd on a carbon support is higher than Pd / C catalyst, however it has also been demonstrated that the Au / C catalyst offers greater selectivity than either the pure palladium or bimetallic catalysts. While on the basis of yield of hydrogen peroxide the Au-Pd / C catalyst is shown to be the most efficient.<sup>78</sup>

For any large scale application of the direct synthesis process, catalyst cost is an important factor that must be considered and any reduction in cost, while maintaining efficiency would be of great benefit. The replacement of costly precious metals such as Au or Pd with readily abundant, less costly base metals would offer significant savings upon scaling of the process to an economically viable size. Hutchings and co-workers<sup>80</sup> have recently reported a series of Pd-base metal catalysts, which are completely selective towards the direct synthesis of  $\text{H}_2\text{O}_2$ . Through successive heat treatments it has been shown that the degradation of  $\text{H}_2\text{O}_2$  can be completely inhibited. The detailed investigation of a 3 wt. % Pd – 2 wt. % Sn /  $\text{TiO}_2$  catalyst that has been exposed to this optimized heat treatment cycle has yielded an approach that is believed to be applicable to a number of other Pd- base metal combinations, including Ni, Zn, Ga, In and Co.

Hutchings and co-workers<sup>79</sup> have provided much evidence that after an oxidation – reduction – oxidation (O-R-O) heat treatment the small Pd-rich nanoparticles responsible for  $\text{H}_2\text{O}_2$



degradation are encapsulated into a SnO<sub>x</sub> layer limiting catalytic activity towards H<sub>2</sub>O<sub>2</sub> destruction, possibly by reducing the availability of low coordination Pd edge sites. The larger uncovered Pd-Sn alloy nanoparticles are believed to be responsible for the formation of H<sub>2</sub>O<sub>2</sub>. Through this O-R-O treatment it is possible to produce a catalyst that is highly selective, stable and active; all key criteria for any possible industrial application. As can be seen in Figure 1.10 there is no loss of activity with sequential catalyst use; that is the replacement of reactant gas and it is possible to achieve relatively high concentrations of H<sub>2</sub>O<sub>2</sub> through subsequent reactions. For any commercial application catalyst activity must be stable over multiple uses and offer high selectivity towards H<sub>2</sub>O<sub>2</sub> and the 3 wt. % Pd – 2 wt. % Sn / TiO<sub>2</sub> catalysts reported by Hutchings and co-workers fulfill both of these requirements and may form the basis of any large scale development of the direct synthesis of H<sub>2</sub>O<sub>2</sub>.

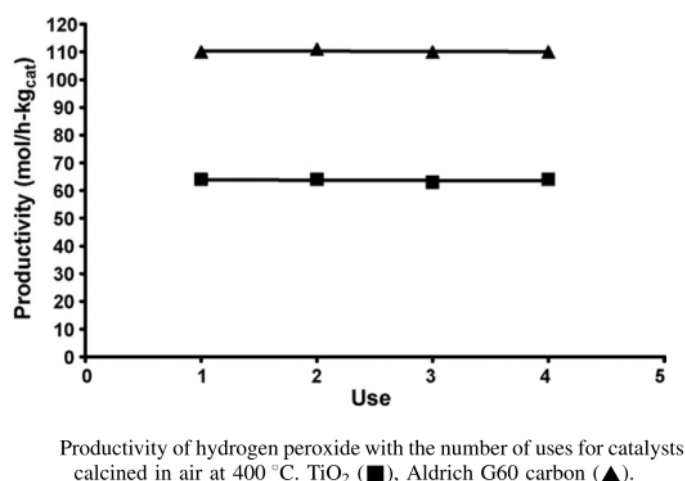


**Figure 1.10.** Sequential H<sub>2</sub>O<sub>2</sub> synthesis reactions utilising a Sn-Pd / TiO<sub>2</sub> catalyst subjected to optimised O-R-O heat treatment.<sup>79</sup>

### 1.9. The effect of the calcination process on the effectiveness of bimetallic catalysts in the direct formation of hydrogen peroxide.

It has been observed<sup>62</sup> that the effect of calcination is vital for ensuring catalyst stability and re-usability, which is a key economic and environmental aspect. Uncalcined bimetallic catalysts offer greater activity towards hydrogen peroxide synthesis and high hydrogen conversions are observed for these catalysts. However these catalysts are intrinsically unstable and it is possible that the active metal components may leach from the catalyst support and reportedly approximately 90 % of the active metal component is lost upon a second use of the catalyst.<sup>80</sup> Interestingly this has been attributed as the reason for the higher activity of the uncalcined catalysts as a homogeneous catalyst is formed.<sup>16</sup> In

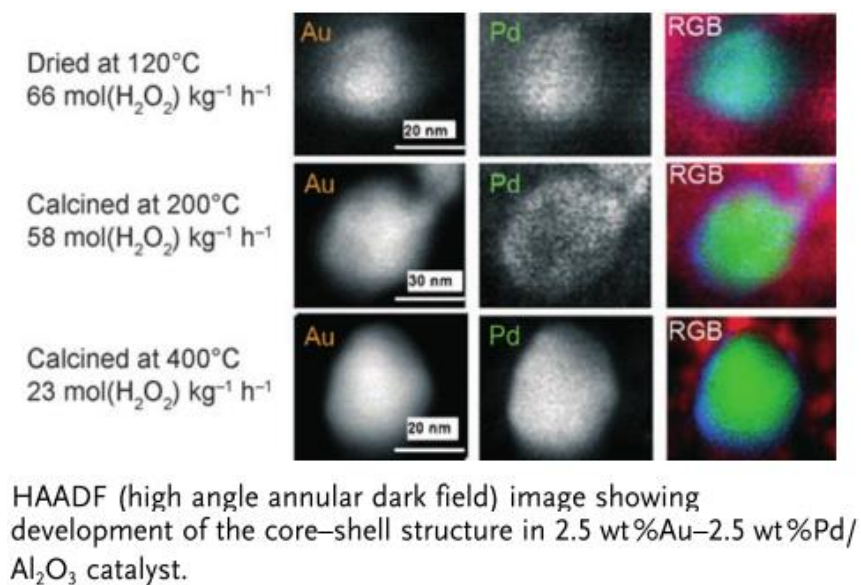
comparison to their uncalcined counterparts those catalysts calcined at 400 °C offer greater stability and are still active after a number of uses as seen in Figure 1.11. Indeed it has been reported that catalysts have been used up to ten times without loss of performance and without leaching of any of the active metals. The role of calcination has been further investigated by Menegazzo *et.al.*<sup>55</sup> who report the calcination step is mandatory for the production of a stable catalyst.



**Figure 1.11.** The effect of the calcination process in maintaining catalytic efficiency for 2.5 wt. % Au -2.5 wt. % Pd / TiO<sub>2</sub> (squares) / C (triangles) towards the direct synthesis of H<sub>2</sub>O<sub>2</sub>.<sup>16</sup>

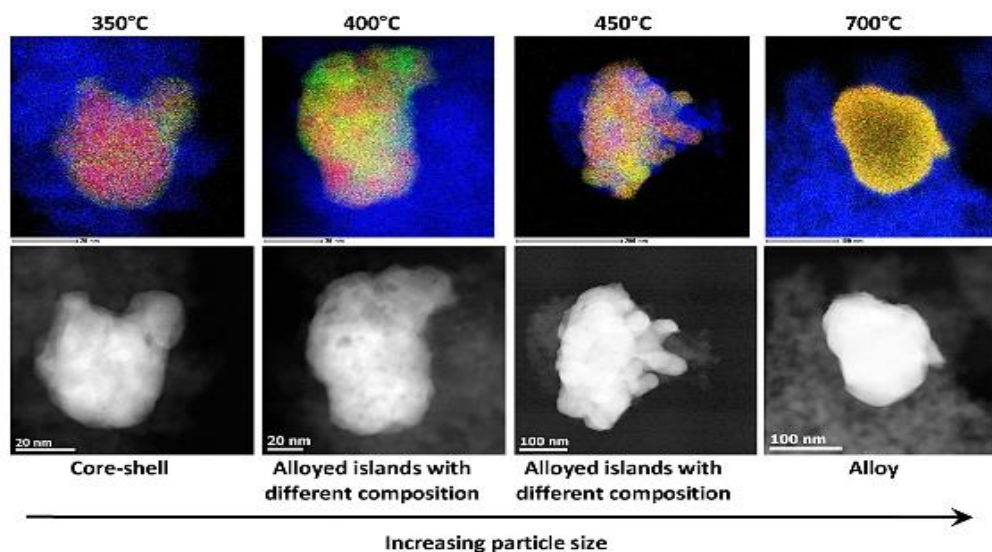
Interestingly as calcination temperature increased the activity of the bimetallic Au-Pd catalysts supported on Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> decreased while the activity of the SiO<sub>2</sub> supported catalyst showed an increase with calcination temperature up to 300 °C. However at a calcination temperature of 400 °C the catalyst became drastically less active and this has been ascribed to the sintering of the nanoparticles,<sup>16</sup> thus producing larger nanoparticles.

The development of larger metal nanoparticles has been suggested to be the attribute responsible for lower catalytic activity, with larger particles being associated with lower activity, both towards H<sub>2</sub>O<sub>2</sub> synthesis and hydrogenation / decomposition.<sup>81</sup> As can be seen from the HAADF image in Figure 1.12, of 2.5 wt. % Au - 2.5 wt. % Pd / Al<sub>2</sub>O<sub>3</sub>, as calcination occurs and then the temperature of calcination increase the morphology of the Au-Pd alloys moves from a homogeneous alloy, seen in the dried sample, to a core-shell structure when calcined, with a PdO-rich shell and an Au rich core. This morphology has been reported on a number of oxide supports, while it has been demonstrated that the metal nanoparticles on a carbon support exhibit a random alloying, rather than core-shell morphology.



**Figure 1.12.** The development of core-shell morphology with calcination temperature.<sup>81</sup>

Cybula *et.al*<sup>82</sup> have investigated the effect of calcination temperature on TiO<sub>2</sub> modified with Au-Pd, they report that as calcination temperature increased from 350 to 700 °C the surface Pd to Au ratio changes from 5 : 1 to 1 : 4, as well as led to an increase in nanoparticle size. This is particularly interesting as it suggests catalyst activity can be tuned through the use of calcination temperature. It is reported that as calcination temperature increases the nanoparticles move from a Au core – PdO shell morphology to an island like structure, with areas of different composition. Figure 1.13 follows the effect of calcination temperature on the Au-Pd nanoparticles via HAADF combined with elemental mapping. It is possible to observe the development of the Au-enriched surface as calcination temperature increases. It is suggested that the gold-enrichment in the shell region of the Au-PdO bimetallic nanoparticle observed by the authors may allow for the design of more selective catalysts for the direct synthesis of H<sub>2</sub>O<sub>2</sub>.



**Figure 1.13.** HAADF images combined with elemental mapping of Au-Pd modified TiO<sub>2</sub>. Au (red), Pd (green) and Ti (blue) calcined at 350 400 and 700 °C.<sup>82</sup>

### 1.10. Particle morphology in bimetallic Au-Pd supported catalysts.

It has been reported that the calcination process aids in the alloying of Au and Pd<sup>16</sup> and so it was of interest to determine the nature of the metals in the Au - Pd supported catalysts, that is if the metal components existed separately or as an Au-Pd alloy and a number of studies have been undertaken to determine this.<sup>81</sup>

It is possible to collect the various supports into two groups; the metal oxides and carbon, with a difference in morphology of the metal nanoparticles seen between these two. The metal oxide supported catalysts have been shown to exhibit core-shell structures with PdO-rich shells and Au-rich cores<sup>16, 80, 83</sup> upon calcination. Although it should be noted that the silica supported catalyst morphology is yet to be determined. Findings from Hutchings and co-workers have shown this to be the case when comparing 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> and 2.5 wt. % Au – 2.5 wt. % Pd / carbon catalysts and, further studies of Au-Pd nanoparticles supported on Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> provide further evidence<sup>12,13,83,84</sup>. They have shown that the effect of calcination and also calcination temperature on Au-Pd nanoparticle morphology. A systematic series of Au-Pd / Al<sub>2</sub>O<sub>3</sub> samples, exposed to various heat treatments were studied by STEM-XEDS imaging. From this data it was possible to determine that the uncalcined (dried at 120 °C) catalyst shows homogeneous Au-Pd nanoparticles while the calcined samples indicate the development of the PdO rich shell, Au rich core morphology and this is seen in Figure 1.12. Hutchings suggests that the preferential

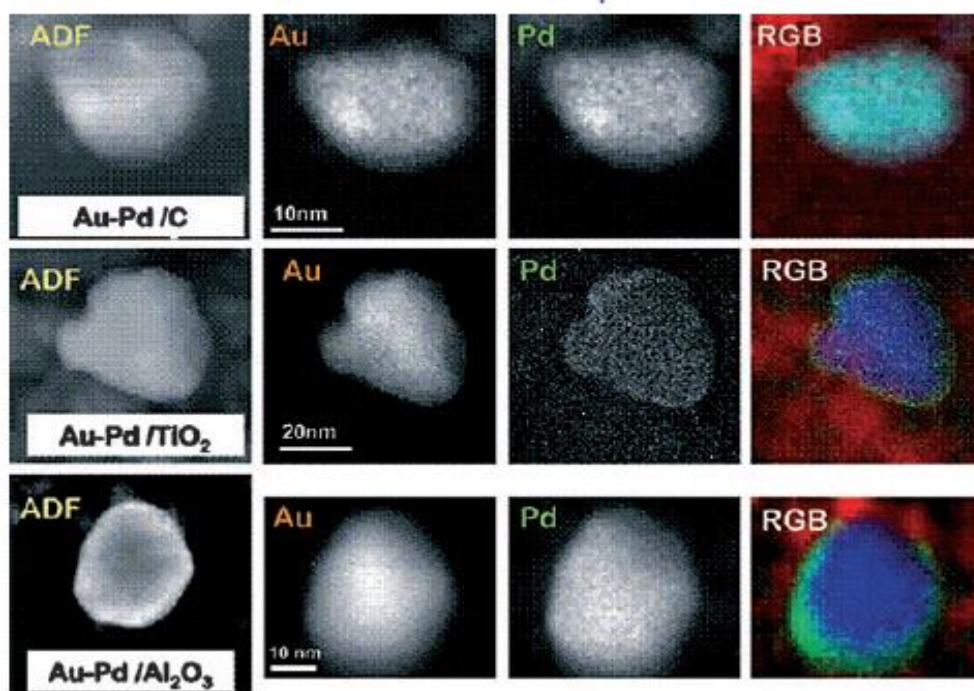
formation of Pd-O bonds at the alloy surface is responsible for palladium surface segregation within the alloy nanoparticles.<sup>81</sup>

The surface of these core-shell structures however will not consist entirely of palladium, as is the case with the 2.5 wt. % Au – 2.5 wt. % Pd / Al<sub>2</sub>O<sub>3</sub> catalyst investigated. If this was true only the activity of the palladium will be observed and this does not occur. In comparison the carbon supported Au-Pd catalyst was shown to retain the random homogeneous alloy nature of the nanoparticles.<sup>80</sup>

The dried only TiO<sub>2</sub> and SiO<sub>2</sub> supported catalysts exhibit an Au:Pd surface ratio (by weight) considerably different from the bulk value of 1:1, in comparison the surface ratio for the carbon and Al<sub>2</sub>O<sub>3</sub> supported catalyst is similar to that of the bulk. It has been observed that upon calcination at 400 °C the surface of AuPd catalysts supported on SiO<sub>2</sub>, TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> catalyst surface become enhanced in palladium in a manner consistent with the formation of core-shell structures. It has been suggested that the adoption of this core-shell morphology is responsible for the enhancement in the stability of the catalyst upon calcination at 400 °C<sup>50</sup> and the formation of core shell structures is believed to be due to the preferential formation of PdO over Au<sub>2</sub>O<sub>3</sub> in temperatures of approximately 400 °C which in turn may be responsible for palladium surface segregation<sup>85</sup>.

Hutchings and co-workers<sup>81</sup> have suggested that the spontaneous formation of the core shell morphology of Au-Pd catalyst supported on oxide supports is due to the oxidation efficiency of the support surface. As carbon is a reducing support the process of core-shell formation, which is attributed to the formation of PdO species and subsequent surface segregation is deterred.

Figure 1.14 compares the morphology of the Au-Pd nanoparticles on oxide supports to that observed on carbon. It can be seen that upon calcination of the oxide supported catalysts at a temperature of 400 °C, in static air, the Au-core PdO-shell morphology develops. While when a carbon supported Au-Pd catalyst undergoes heat treatment the random homogeneous alloys present upon drying are retained<sup>80</sup>.



**Figure 1.14.** Montage of HAADF images (column 1) Au map (column 2), Pd map (column 3) and GF reconstructed overlay map (column 4; Au blue, Pd green) for calcined AuPd/C (row 1) calcined AuPd/TiO<sub>2</sub> (row 2) and calcined AuPd/Al<sub>2</sub>O<sub>3</sub> (row 3).<sup>80</sup>

Interestingly the carbon supported Au-Pd catalyst was shown to exhibit a tri-modal particle distribution<sup>81</sup> although all particles were Au-Pd alloys. The smallest particles fell in the range 2-5 nm, the intermediary particles between 10 and 20 nm and the larger particles were greater than 100 nm in diameter, although particles of this size were uncommon. However, the particles do exhibit a change in the Au : Pd ratio, however as particle size increases the Pd : Au ratio decreases. The particles between 10-20 nm show the greatest similarity to the Au : Pd surface ratio exhibited by those supported on TiO<sub>2</sub> and SiO<sub>2</sub>.<sup>81</sup>

Rossi and co-workers<sup>86</sup> have investigated the behavior of Au-Pd core-shell nanoparticles in the selective oxidation of benzyl alcohol. A significant improvement in catalytic conversion is observed when using a 10 : 1 (Au : Pd) ratio, a composition corresponding to the amount of Pd required to cover the existing Au cores with a monolayer of Pd. Density functional theory calculations indicate that both the number of active sites and the ease of product desorption is sensitive towards Pd content. It is suggested that these findings may prove significant for further development of Au-Pd catalysts for the direct synthesis of H<sub>2</sub>O<sub>2</sub>.

Further investigation into Au – Pd catalysts supported on SiO<sub>2</sub> by Strukul and co-workers<sup>88</sup> has revealed that the choice of catalyst preparation technique is able to improve selectivity

towards  $\text{H}_2\text{O}_2$ . Comparison of incipient wetness co-impregnation and consecutive incipient wetness impregnation reveals that the former technique is able to produce catalysts with greater activity and selectivity towards  $\text{H}_2\text{O}_2$ . Indeed catalytic selectivities for the co-impregnation and consecutive impregnation are reported as 53 % and 47 % respectively. The authors report that the choice of preparation technique can induce different metal interactions as well as different particle morphologies, with preparation via the co-impregnation technique providing mixed Au-Pd alloyed nanoparticles, where the presence of Au is able to enhance the formation of PdO. In comparison preparation of catalysts utilizing consecutive incipient wetness impregnation does not give rise to these mixed metal nanoparticles and as a result Pd is found to be present in the metallic  $\text{Pd}^0$  oxidation state. It is suggested that the presence of the AuPdO phase is able to ensure the availability of less energetic catalytic sites necessary to activate the  $\text{O}_2$  molecule without cleavage of the O-O bond.

### **1.11. The role of the support in the direct synthesis of $\text{H}_2\text{O}_2$ .**

A variety of supports have been utilised in the direct synthesis of hydrogen peroxide from hydrogen and oxygen. The state of the support shows discernible influence on the formation of hydrogen peroxide as well as competing routes, particularly the hydrogenation of hydrogen peroxide and combustion of hydrogen. The performance of the supported catalyst is generally governed by several factors, including metal particle size, shape, morphology, the dispersion of the metal particles and the electronic state of the support<sup>11</sup>. However Choudhary and co-workers<sup>74</sup> have shown that particle size and surface area of palladium-only catalyst are less important than the oxidation state in determining hydrogen peroxide selectivity.

The most common supports that have been studied for the direct synthesis of hydrogen peroxide are carbon, silica, alumina, silica-alumina and titanium dioxide has been studied.<sup>89,90</sup> The reactivity of varying supports for Au-Pd supported catalysts has been investigated and the order of reactivity has been found to be carbon >  $\text{TiO}_2$  >  $\text{SiO}_2$  >  $\text{Al}_2\text{O}_3$  >  $\text{Fe}_2\text{O}_3$ . Interestingly Ishihara *et.al.*<sup>90</sup> have demonstrated that gold-palladium catalysts supported on  $\text{TiO}_2$  with the rutile structure offers greater selectivity and activity towards hydrogen peroxide synthesis than either the anatase- $\text{TiO}_2$  or mixed rutile and anatase P-25- $\text{TiO}_2$  support. It is also revealed that the surface composition of active components and metal

particle morphology play a more important role in governing catalysts activity and selectivity in comparison to surface area of the support. Evidence for this came from comparison of P-25-TiO<sub>2</sub> and rutile-TiO<sub>2</sub> as supports for gold-palladium catalysts. The rutile-TiO<sub>2</sub> has a significantly smaller surface area than the mixed analogue but was seen to be more active for hydrogen peroxide formation.

It has been shown that the presence of acidic reaction conditions has beneficial effects of the catalyst with regards to H<sub>2</sub>O<sub>2</sub> yield.<sup>91</sup> Furthermore it has been reported that accelerated reactor corrosion is a concern when using acidic additives. Therefore acidic supports, with lower isoelectric points, are receiving attention as a potential replacement for the more common supports.

The isoelectric point of the support has been shown to be an important factor for hydrogen peroxide synthesis<sup>83</sup>, with supports with a lower isoelectric point offering the highest rate of H<sub>2</sub>O<sub>2</sub> synthesis and lowest rate of hydrogen peroxide decomposition and hydrogenation. It is known that the support's isoelectric point controls its surface charge, and as basic supports favor the hydrogenation of hydrogen peroxide<sup>83</sup> it is preferential to utilize supports of a more acidic nature in the direct synthesis of hydrogen peroxide. Indeed the rate of H<sub>2</sub>O<sub>2</sub> hydrogenation and decomposition has been reported at 206 and 217 molKg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> for the MgO support alone, prior to the impregnation of metals, such as Pd and Au.<sup>83</sup> Table 1.5 compares the activity of various supports, with no metal incorporation towards H<sub>2</sub>O<sub>2</sub> synthesis and degradation. According to these findings supports of carbon and silica should give catalyst that provides the greatest rate of synthesis of H<sub>2</sub>O<sub>2</sub>, with productivity values of 110 mol<sub>H2O2</sub>Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> reported for 2.5 wt. % Au – 2.5 wt. % Pd / C catalyst; while TiO<sub>2</sub>, with an isoelectric point of approximately 6.5 is reported to have a productivity value of 64 mol<sub>H2O2</sub>Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>.<sup>68</sup>



**Table 1.5.** Comparison of the activity of various supports to the direct synthesis and degradation of H<sub>2</sub>O<sub>2</sub>.

Support	H <sub>2</sub> O <sub>2</sub> hydrogenation/ mol <sub>H<sub>2</sub>O<sub>2</sub></sub> Kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	H <sub>2</sub> O <sub>2</sub> decomposition /mol <sub>H<sub>2</sub>O<sub>2</sub></sub> Kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	H <sub>2</sub> O <sub>2</sub> productivity/ mol <sub>H<sub>2</sub>O<sub>2</sub></sub> Kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>
Al <sub>2</sub> O <sub>3</sub> <sup>12</sup>	0	0	0
TiO <sub>2</sub> <sup>15</sup>	0	0	0
MgO <sup>82</sup>	206	217	0
Carbon <sup>82</sup>	94	24	0
Cs <sub>2.8</sub> H <sub>0.2</sub> PW <sub>12</sub> O <sub>40</sub> <sup>22</sup>	162	<i>n.d.</i>	1

**Reaction Conditions:** As outlined in Table 1.2.**n.d.** = not determined

Hutchings initial discovery of the synergistic effect and subsequent advantages of Au-Pd supported catalysts has led to extensive study of this catalytic system in particular those catalysts on carbon<sup>8</sup> and oxide supports have received much attention (Al<sub>2</sub>O<sub>3</sub><sup>12</sup>, SiO<sub>2</sub><sup>53</sup> TiO<sub>2</sub><sup>15</sup> Fe<sub>2</sub>O<sub>3</sub><sup>13</sup> and MgO<sup>52</sup>) as well as Zeolite-Y and HZSM-5<sup>65</sup>, the results of which are summarized in Table 1.6. It was found that carbon<sup>52</sup> was the best support, providing the highest hydrogen peroxide productivity and lowest rates of hydrogenation and decomposition.

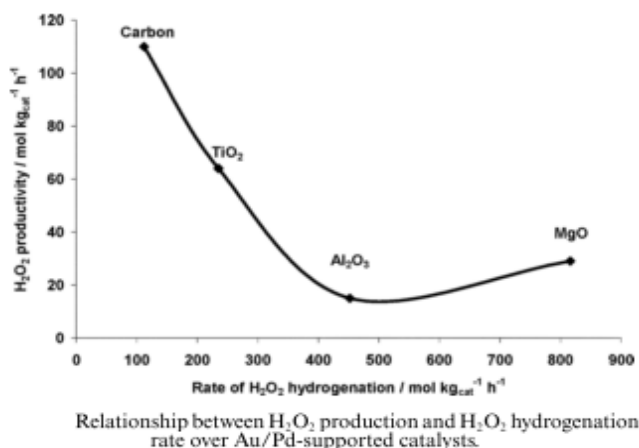
**Table 1.6.** Effect of the support on hydrogenation, decomposition and synthesis over Au-Pd catalysts.

Catalyst, 5 wt. %	Hydrogenation / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> Kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> <i>a</i>	Decomposition / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> Kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> <i>b</i>	Productivity / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> Kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> <i>c</i>	H <sub>2</sub> Selectivity / (%) <sup>d</sup>
1 : 1 (Au : Pd)				
Au-Pd/Al <sub>2</sub> O <sub>3</sub> <sup>12</sup>	452	59	15	14
Au-Pd/TiO <sub>2</sub> <sup>15</sup>	235	129	64	70
Au-Pd/MgO <sup>52</sup>	817	535	29	38
Au-Pd/C <sup>5</sup>	117	41	110	80
Au-Pd /γ <sup>65</sup>	<i>n.d.</i>	<i>n.d.</i>	89	<i>n.d.</i>
Au-Pd / HZSM- 5 <sup>65</sup>	<i>n.d.</i>	<i>n.d.</i>	52	<i>n.d.</i>

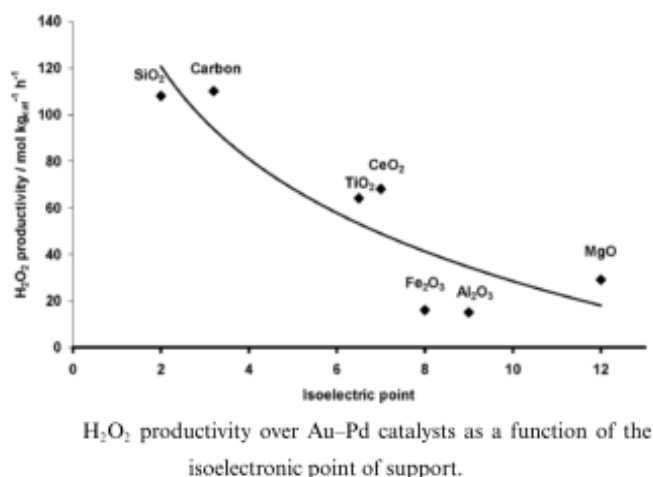
**Reaction Conditions:** As outlined in Table 1.2.**n.d.** = not determined.

Figure 1.15 compares the isoelectric point of the supports, catalytic productivity and hydrogenation activity for bimetallic 2.5 wt. % Au- 2.5 wt. % Pd supported catalysts. There is an inverse correlation between the rates of H<sub>2</sub>O<sub>2</sub> production and hydrogenation and bimetallic catalysts that have a high rate of H<sub>2</sub>O<sub>2</sub> synthesis have a low rate of hydrogenation and decomposition. From Figures 1.15 and 1.16 below it can be seen that the reason for the

poor catalytic performance of the MgO-supported bimetallic catalyst is related to the loss of catalyst selectivity due to the high rates of the subsequent hydrogenation and decomposition reactions.



**Figure 1.15.** Comparison of catalytic activity of Au-Pd supported catalysts towards  $\text{H}_2\text{O}_2$  synthesis and hydrogenation.<sup>52</sup>



**Figure 1.16** Comparison between the activity of bimetallic Au-Pd catalysts on various supports towards the formation of hydrogen peroxide and the isoelectric point of the support.<sup>52</sup>

Hutchings and co-workers<sup>52</sup> have shown that the support is critical in determining the performance of the catalyst for the direct synthesis of hydrogen peroxide as it controls the dispersion of the Au and Pd components as well as providing the sites that are responsible for the subsequent hydrogenation and decomposition of  $\text{H}_2\text{O}_2$ . As such it is possible to improve catalytic selectivity through the choice of catalyst support.

This has further been discussed by Menegazzo *et.al.*<sup>55</sup> who have reported that it is possible to control Pd nanoparticle size and in turn balance catalytic activity and selectivity towards

H<sub>2</sub>O<sub>2</sub> through the choice of support. They report that the use of SiO<sub>2</sub> is superior to that of either ZrO<sub>2</sub> or CeO<sub>2</sub> in tuning these two parameters of catalytic efficiency. Again this may be related to the isoelectric point of the support, as seen in Figure 1.16 for the SiO<sub>2</sub> and CeO<sub>2</sub> supported AuPd catalysts.

The effects of acid additives in improvement of monometallic Pd supported catalysts, through inhibition of base-catalyzed decomposition and improvement in selectivity has been previously reported.<sup>51</sup> In order to further improve catalytic selectivity Hutchings and co-workers<sup>8</sup> have studied the effect of acid pre-treatment of carbon supported Au-Pd catalysts in the direct synthesis of hydrogen peroxide. It was found that acid treatment of the supports prior to metal dispersion is crucial in producing a catalyst that has low activity towards hydrogen peroxide hydrogenation and thus enhanced selectivity. It has been demonstrated that the process of acid pre-treatment of the support favors the formation of smaller, Pd rich, nanoparticles at the expense of those nanoparticles with larger Au content. Therefore gold dispersion is enhanced, as smaller nanoparticles form and these are then able to decorate support sites that are active for the hydrogenation of hydrogen peroxide.<sup>8</sup> The observation that the smaller, Pd rich nanoparticles are associated with higher catalytic activity is in agreement with other investigations into bimetallic catalysts.<sup>74</sup>

Interestingly the alteration in particle size distribution and subsequent inhibition of the hydrogenation sites of the support is only observed in bimetallic Au-Pd and monometallic Au-only supported catalysts. It has therefore been suggested that the alloying of Au is necessary to observe the redistribution of particle size. Hutchings<sup>84</sup> has attributed this to the electronic structure of Pd being influenced by Au in a manner that the hydrogenation activity is inhibited. This suggestion is in keeping with the work of Han *et.al.*<sup>72</sup>

Hu and co-workers<sup>92</sup> have demonstrated that a correlation exists between catalytic performance and the structure and physiochemical properties of the support. Through comparison of a number of carbon materials as supports for Pd they have demonstrated that the presence of an ordered graphitic structure, in addition to lower concentrations of surface carboxylic (-COOH) groups, favors catalytic selectivity towards H<sub>2</sub>O<sub>2</sub>. The presence of carboxylic groups on the support are shown to increase the rates of H<sub>2</sub>O<sub>2</sub> hydrogenation and decomposition. It is suggested by the authors that the presence of these functional groups on the surface of the support increases the hydrophilicity of the catalyst and that H<sub>2</sub>O<sub>2</sub>

formed over this catalyst can be re-adsorbed onto the surface, leading to the subsequent degradation of  $\text{H}_2\text{O}_2$ .

Ao *et.al.*<sup>93</sup> have reported that the selectivity of  $\text{TiO}_2$  supported Pd catalysts can be improved if the  $\text{TiO}_2$  support was doped with nitrogen before Pd deposition followed by treatment under different atmospheres. Investigation in to catalyst selectivity towards  $\text{H}_2\text{O}_2$  is reported to increase from 61 % for the undoped 1 wt. % Pd /  $\text{TiO}_2$  catalyst to 75 % for the 1 wt. % Pd / N-doped  $\text{TiO}_2$  catalyst exposed to a  $\text{N}_2$  atmosphere, while there is a slight decrease in selectivity upon exposure of the 1 wt. % Pd / N-doped  $\text{TiO}_2$  catalysts to  $\text{O}_2$  and  $\text{H}_2$ , to 59 and 55 % respectively. It is reported that there is no change in mean diameter of the Pd nanoparticles, with a particle size of approximately 2 nm reported for both the N-doped and unmodified  $\text{TiO}_2$  supported catalysts. However, the atomic ratio of  $\text{Pd}^0 : \text{Pd}^{2+}$  is reported to decrease from 1.1 for the 1 wt. % Pd /  $\text{TiO}_2$  catalyst to 0.47 for the 1 wt. % Pd / N-doped  $\text{TiO}_2$  catalyst exposed to a  $\text{N}_2$  atmosphere, with a resulting increase in catalytic selectivity. In comparison exposure of the 1 wt. % Pd / N-doped  $\text{TiO}_2$  catalyst to a  $\text{H}_2$  or  $\text{O}_2$  atmosphere increases the  $\text{Pd}^0 : \text{Pd}^{2+}$  to 2.5 and 2.3 for the catalysts supported on N-doped  $\text{TiO}_2$  exposed to  $\text{H}_2$  and  $\text{O}_2$  respectively with the resulting decrease in catalyst selectivity. The authors suggest that doping N into  $\text{TiO}_2$  in different atmospheres can lead to the formation of oxygen vacancies, which are substituted by  $\text{N}_{\text{ad}}$  and  $\text{O}_{\text{ad}}$  species. The former favors the fixation of Pd atoms and the latter results in the adsorbed oxygen on  $\text{TiO}_2$ . The synergistic effects of the two factors are responsible for a volcano-like curve of the ratio of  $\text{Pd}^0 : \text{Pd}^{2+}$  resulting in the different catalytic performances of the 1 wt. % Pd / N-doped  $\text{TiO}_2$  catalysts. Likely more metallic Pd atoms on the surface of the catalyst favor the direct synthesis of  $\text{H}_2\text{O}_2$  while side reactions are suppressed on  $\text{Pd}^{2+}$  rich surfaces.

### **1.12. The role of additives in the direct synthesis of hydrogen peroxide.**

One of the major problems associated with the direct synthesis of  $\text{H}_2\text{O}_2$  is that the catalysts used also show catalytic activity towards decomposition and hydrogenation of  $\text{H}_2\text{O}_2$ , as well as oxidation of hydrogen to water. These three unwanted side reactions cause a decrease in selectivity and yield of hydrogen peroxide and are therefore it is of great interest to inhibit these pathways.

Several studies <sup>19, 46,88,94-96</sup> have reported that the presence of halides within the reaction medium; either as an alkali metal salt, halogen acid or conversely incorporated directly into the catalyst, cause an increase in the selectivity of catalysts towards H<sub>2</sub>O<sub>2</sub>. This is believed to be due to the halide acting as catalyst inhibitor for decomposition of H<sub>2</sub>O<sub>2</sub> to water.

The effect of the halides in palladium catalysed, direct synthesis of H<sub>2</sub>O<sub>2</sub> can be associated with their  $\sigma$  or  $\pi$  donation ability. The availability of halide electrons, and their capability to form  $\sigma$  bonds increases down the group. It is therefore expected that iodide will form the strongest bonds and donate the most electron density to the metal, if no other halide metal interactions were present. However it is also common for  $\pi$  interactions to occur between the halide lone pair of electrons and the metal d-orbitals. This results in the opposite trend for electron donation to that above. The intermediate halides in particular have been shown to be highly suitable in the promotion of hydrogen peroxide selectivity<sup>11</sup>.

The nature of the palladium-halide interaction has been shown to be very important in controlling the selective oxidation of hydrogen to hydrogen peroxide.<sup>31</sup> Catalysts where the palladium is oxidised and therefore have PdO-X interactions, where X is Cl<sup>-</sup> or F<sup>-</sup>, have been shown to have lower activity for hydrogen peroxide decomposition than those catalysts that have Pd<sup>0</sup>-X interactions. It is worth noting that Br<sup>-</sup> is a suitable promoter of hydrogen peroxide selectivity regardless of the oxidation state of palladium.<sup>74</sup>

Choudhary and co-workers<sup>3</sup> have demonstrated that bromination of various supported palladium catalysts provides an increase in selectivity and yield of hydrogen peroxide. Further investigation by Lunsford and Liu<sup>97</sup> suggested that the presence of Cl<sup>-</sup> or Br<sup>-</sup> inhibit hydrogen peroxide reduction, possibly due to the blocking of catalytic sites that would facilitate the breaking of O-O bonds.<sup>19,98</sup> This prevents the non-selective combustion of hydrogen to water as well as decomposition and reduction of hydrogen peroxide. The work of Lunsford and co-workers<sup>99</sup> have also shown that Br<sup>-</sup> is more effective than Cl<sup>-</sup>, on a molar basis, in promoting hydrogen peroxide formation. Bromide ions are known to block the active site of palladium catalysts responsible for the combustion of hydrogen to water and the disproportionation of hydrogen peroxide. However it has also been shown that an optimum amount of Br<sup>-</sup> is required, when present in excess Br<sup>-</sup> indiscriminately blocks

catalytically active sites thus inhibiting hydrogen conversion to hydrogen peroxide and in so doing decreases the net formation of hydrogen peroxide<sup>3</sup>.

Interestingly Choudhary *et.al.*<sup>94</sup> have revealed that the incorporation of two halides, when the first is bromine and the second is either chlorine or fluorine, offer greater hydrogen peroxide productivity than either of the halides alone. This is believed to be due to the synergistic effects of combining two halides, which interact to alter the electronic properties of palladium clusters in the catalyst. As eluded to above this synergistic effect is greatest when the two halides differ greatly in electronegativity. It is believed that the effect of the two halides is to inhibit O-O bond cleavage of oxygen and hydrogen peroxide and in doing so reducing the rate of hydrogen combustion, hydrogen peroxide decomposition and hydrogenation reactions.

X-ray absorption fine structure spectroscopy (EXAFS) characterization of Pd supported on the commercial resin K2621 under reaction conditions (*in-situ*) by Centomo *et.al.*<sup>75</sup> reveals that the role of bromide ions as enhancers of the selectivity of supported Pd catalysts cannot be limited to the selective blocking of active sites responsible for the degradation of H<sub>2</sub>O<sub>2</sub> to water. The authors report that the inclusion of NaBr (10 ppm) to the reaction mixture is able to increase the atomic fraction of PdO from 62 to 76 % as well as promotes the leaching of Pd from the support and it is suggested that both of these factors contribute to the improved H<sub>2</sub>O<sub>2</sub> selectivity observed when bromides (or chlorides) are used as additives for the direct synthesis process.

However it has been demonstrated that the presence of only halide ions is not sufficient for the promotion of the selective oxidation of hydrogen to hydrogen peroxide<sup>11</sup>, particularly for palladium only catalysts. When present with H<sup>+</sup> ions selectivity towards hydrogen peroxide is greatly enhanced. The presence of H<sup>+</sup> in the reaction mixture has been found to be crucial for achieving higher hydrogen peroxide selectivity and productivity<sup>51</sup> this is attributed to the pH of the reaction medium being lower than the catalyst support's isoelectric point. This ensures that it is only the halide anions, and not their associated cations, that are able to adsorb onto the palladium surface. The adsorption of the halides, as stated above alters the electronic environment of the catalyst surface. Choudhary<sup>100</sup> has shown that this modification occurs through the measurement of binding energies of the Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub> electrons. These values decreased significantly after the catalysts (with a KBr promoter)

were used in hydrogen to hydrogen peroxide oxidation, indicating that the electronic nature of the palladium had been altered. In addition, these findings suggest that the adsorbed bromide anions are either close to the palladium particles in the catalyst or mobile on the catalyst surface during the reaction in order to interact with the palladium. It should also be noted that in the absence of protons it is possible that the halide promoter may cause an increase in hydrogen peroxide decomposition, particularly when the halide is iodine.<sup>101</sup>

Several studies<sup>62,100</sup> have shown that when protons are present in the reaction medium, without the presence of halide, palladium catalysts show little selectivity for H<sub>2</sub>O<sub>2</sub> formation. However, when both halide anions and protons are present in the reaction solution the catalyst shows both high selectivity and activity for H<sub>2</sub>O<sub>2</sub> formation. Therefore both protons and halide are required in partnership in order for a catalyst to be efficient for the direct synthesis of hydrogen peroxide.

It is interesting to note that the presence of protons alone have been shown to inhibit H<sub>2</sub>O<sub>2</sub> decomposition<sup>11</sup>. These observations indicate that in the presence of protons, but the absence of halide anions the combustion reaction dominates, rather than hydrogenation or decomposition, as the major competitive reaction to H<sub>2</sub>O<sub>2</sub> synthesis with these individual pathways outlined in Figure 1.1.

A number of classes of acids have been investigated as a proton source in the direct synthesis of hydrogen peroxide, including oxoacids (H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>) and haloacids (HCl, HBr, HI). It was discovered by Choudhary and Samanta<sup>88</sup> that the presence of an oxoacid did cause a small increase in hydrogen conversion however, very little H<sub>2</sub>O<sub>2</sub> was produced. This result was found to be comparable for all oxoacids and clearly shows the importance of protons over their associated anions. However the presence of protons alone is not enough to encourage selective oxidation of H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>. For this to occur halo-acids must be utilized and many studies<sup>46,98</sup> have shown that the presence of a halo-acid increases H<sub>2</sub>O<sub>2</sub> yield and productivity to a far greater extent than non-halo acids. In addition to this the effect of acid concentration on hydrogen peroxide decomposition activity has been studied and it has been shown that as acid concentration increases so does the suppression of H<sub>2</sub>O<sub>2</sub> decomposition.<sup>11</sup>

However the use of high quantities of acid has been proposed to be responsible for the dissolution of the active phase from the catalyst, resulting in the formation of an unstable

catalyst and  $\text{H}_2\text{O}_2$ . In addition to this, it has been found that the presence of acid leads to an accelerate corrosion of the reactor<sup>11</sup>. These drawbacks have led to the investigation of acidic supports in the direct synthesis of hydrogen peroxide as an alternative acid additive<sup>8,21,23,48</sup> and the potential for the use of Cs- exchanged tungstophosphoric acid as a replacement for common haloacid additives are explored in Chapter 3.

### **1.11. Heteropolyacid based catalysts in the direct synthesis of hydrogen peroxide.**

It has been reported that the presence of halide and acid prevent hydrogen peroxide decomposition. However the use of acids has been shown to have a detrimental effect on reactor longevity, accelerating the rate of reactor corrosion significantly. It has also been shown that acid additives can cause the leaching of the active metals from the support. In order to overcome these problems, acidic supports have been studied.

Heteropolyacids (HPAs) are inorganic acids with an acid strength stronger than other, solid acids<sup>32</sup> this coupled with their precedence in large scale industrial processes as an oxidation and acid catalyst as well as the environmental benignity<sup>101</sup> has led to HPAs being studied in the direct synthesis of hydrogen peroxide.<sup>102,103</sup> It is known that the protons in Keggin-type tungstophosphoric acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) are almost super-acidic<sup>105</sup>. The high solubility in polar solvents as well as the low surface area ( $< 10 \text{ m}^2/\text{g}$ ) of HPAs, including  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , has been overcome by the introduction of specific cations in to the Keggin structure in exchange for protons. The use of large cations, such as  $\text{Cs}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{NH}_4^+$  has been shown to produce a water-insoluble structure with a considerably higher surface area ( $< 100 \text{ m}^2/\text{g}$ ) than those HPAs which have not undergone cation exchange.<sup>105</sup>

Park and co-workers<sup>105</sup> have reported that the separation of palladium-exchanged insoluble HPAs from a polar solvent is somewhat difficult owing to the small average size of the particles (approximately 10 nm). To overcome this insoluble HPAs have been immobilised on porous materials such as mesoporous silica.<sup>106</sup>

Mesoporous silicas have large uniform pores, in the range of 10-50 nm and a large surface area and it is these attributes which have led to their use in catalysis science and engineering



alike. In particular mesostructured cellular foam (MCF) has been shown to be an efficient support for immobilisation of various large molecules.<sup>103</sup>

Sun *et.al.*<sup>21</sup> have recently shown that Pd based supported heteropolyacid catalysts exhibit higher H<sub>2</sub>O<sub>2</sub> productivity and selectivity than the conventional Pd only catalysts in the absence of promoters and the formation of H<sub>2</sub>O<sub>2</sub> over a 4 hour period was almost one order of magnitude higher than that provided by other catalysts. Summarised in Table 1.7<sup>21</sup>

**Table 1.7.** Catalytic performance of Pd catalyst on various supports for the synthesis of H<sub>2</sub>O<sub>2</sub> in the absence of promoters over a 4 hour period.

Catalyst	H <sub>2</sub> Conversion / %	H <sub>2</sub> O <sub>2</sub> selectivity / %
Pd/SiO <sub>2</sub>	16	5.9
Pd/TiO <sub>2</sub>	15	9.4
Pd/Graphite	21	9.1
Pd/Cs <sub>1.5</sub> H <sub>1.5</sub> PW <sub>12</sub> O <sub>40</sub>	21	67

**Reaction Conditions:** Catalyst (1 wt. % Pd loading, 0.05 g), T = 283 K, H<sub>2</sub> : O<sub>2</sub> : N<sub>2</sub> = 1 : 4 : 1, gas flow rate = 60 cm<sup>3</sup> min<sup>-1</sup>, solvent = ethanol (60 cm<sup>3</sup>), time = 4 h<sup>21</sup>

Again Sun and co-workers<sup>21</sup> have demonstrated that the amount of Cs present in the polyoxometalate is crucial for the effective synthesis of H<sub>2</sub>O<sub>2</sub>. They have showed that as the amount of Cs increases from x = 0.5 to x = 1.5 in Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> the selectivity and productivity of the catalyst towards H<sub>2</sub>O<sub>2</sub> increased, while conversion of hydrogen decreased. However they have also shown that further increase in the amount of Cs (x > 1.5) decreased both the productivity and selectivity of the catalyst. Therefore they have reported that Pd / Cs<sub>1.5</sub>H<sub>1.5</sub>PW<sub>12</sub>O<sub>40</sub> provides the highest H<sub>2</sub>O<sub>2</sub> selectivity and productivity<sup>21</sup>. On the other hand it has also been reported by Okuhara *et.al.*<sup>178</sup> that as Cs content is increased (from x = 2 to x = 3) the surface area and surface acidity of Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> reaches a maximum and then falls. The effect in surface area can be explained when we consider that a relatively large cation, in this case Cs<sup>+</sup>, is replacing the much smaller H<sup>+</sup>. Surface acidity in this case represents the number of acid sites on the catalyst surface, therefore as surface area increases the number of acid surface sites increases to a point (x = 2.5) as Cs content increases however there is a decrease in proton concentration and so surface acidity decreases. This is an important aspect to consider when designing an effective catalyst as acidic supports have been shown to be effective in reduction of hydrogen peroxide decomposition and it is therefore of interest to utilise a support that is as acidic as possible. The alteration in surface area discovered by Park *et.al.*<sup>108</sup>, measured by BET, with increasing Cs content can be seen in Table 1.8.

**Table 1.8.** The variation of catalytic surface area with varying Cs content.<sup>110</sup>

Value of x in $\text{Pd}_{0.15}\text{Cs}_x\text{H}_{2.7-x}\text{PW}_{12}\text{O}_{40}$	BET surface area ( $\text{m}^2/\text{g}$ )
2.0	30
2.2	57
2.5	105
2.7	125

It has been demonstrated that there is no correlation between catalytic activity and surface area Sun *et al.*<sup>21</sup> have reported that those catalysts with the largest Cs content, and therefore greatest surface area have considerably lower selectivity towards  $\text{H}_2\text{O}_2$  than those supported catalysts with lower Cs content and therefore smaller surface area. Therefore it is the acidity of the support that is expected to be critical in determining catalytic activity.

Park and co-workers<sup>107</sup> have also compared  $\text{Pd}_{0.15}\text{Cs}_{2.5}\text{H}_{0.2}\text{W}_{12}\text{O}_{40}$  and  $\text{Pd} / \text{Al}_2\text{O}_3$  catalysts in the presence and absence of an acidic promoter ( $\text{H}_2\text{SO}_4$ ) and has shown that  $\text{Pd}_{0.15}\text{Cs}_{2.5}\text{H}_{0.2}\text{W}_{12}\text{O}_{40}$  has greater selectivity for hydrogen peroxide, yield of hydrogen peroxide and conversion of hydrogen than the alumina supported palladium, in both the presence and absence of the promoter. This implies that Cs exchanged HPAs are an effective source of protons and offer an efficient alternative to the use of acidic additives.

Hutchings and co-workers<sup>23,66</sup> have investigated Au-only, Pd-only and Au-Pd heteropolyacid supported catalysts in the direct synthesis of hydrogen peroxide. These catalysts with various Cs content were compared with a carbon supported Au-Pd catalyst which, under their chosen reaction conditions is the most effective catalyst for  $\text{H}_2\text{O}_2$  synthesis. It was discovered that the Pd-only and bimetallic Au-Pd heteropolyacid supported catalysts showed higher  $\text{H}_2\text{O}_2$  formation activity compared to the analogous carbon supported catalysts.

Interestingly the addition of Au by ion exchange to Pd only heteropolyacids did not change the catalytic performance, which disagrees with the synergistic effect shown where a more common support is used. In comparison the Au-Pd supported heteropolyacid catalysts showed higher catalytic performance which indicates that the method of preparation of the catalyst is crucial in formation of nanoparticles of varying size, location and morphology.

It is highly desirable for industry, from both an economic and environmental view point, that water be used in the direct synthesis of hydrogen peroxide, the use of toxic, environmentally unfriendly and more expensive organic solvents have contributed to the desire to develop an alternative to the indirect AO process. The ability to conduct catalysis at ambient

temperature is of course highly desired by industry and the production of a catalyst for the direct synthesis process that is able to be effective at ambient conditions is a commendable goal for research. To this end Hutchings and co-workers<sup>23,66</sup> have demonstrated that heteropolyacid-based catalysts prepared by ion exchange offer much greater rates of formation of H<sub>2</sub>O<sub>2</sub> than the Au-Pd- supported heteropolyacid and carbon- based supports prepared by impregnation, illustrated in Table 1.9. Additionally the rate of hydrogenation of the ion exchanged HPA catalysts is much smaller than that of the Pd-Au catalyst supported on heteropolyacid and has comparable hydrogenation rates to that shown by the carbon supported catalyst.

**Table 1.9.** H<sub>2</sub>O<sub>2</sub> productivity and degradation using Au-Pd-exchanged heteropolyacid and Au-Pd supported catalysts at 20 °C using H<sub>2</sub>O as a solvent.<sup>66</sup>

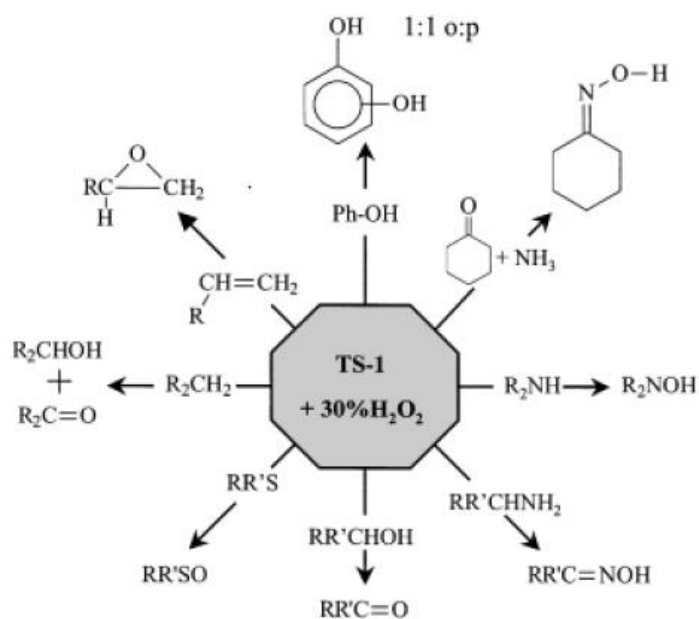
Catalyst	H <sub>2</sub> O <sub>2</sub> Productivity / mol <sub>H2O2</sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> <sup>a</sup>	H <sub>2</sub> O <sub>2</sub> Degradation / mol <sub>H2O2</sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> <sup>b</sup>
2.5%Au-2.5%Pd/ Cs <sub>2.8</sub> H <sub>0.2</sub> PW <sub>12</sub> O <sub>40</sub>	3	1310
2.5%Au-2.5% Pd / Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub>	11	1310
2.5%Au-2.5% Pd / Rb <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub>	10	1205
Pd <sub>0.075</sub> Au <sub>0.05</sub> Cs <sub>2.5</sub> H <sub>0.2</sub> PW <sub>12</sub> O <sub>40</sub>	61	776
Pd <sub>0.075</sub> Au <sub>0.05</sub> Rb <sub>2.5</sub> H <sub>0.2</sub> PW <sub>12</sub> O <sub>40</sub>	49	2302
Pd <sub>0.1</sub> Au <sub>0.0333</sub> Cs <sub>2.5</sub> H <sub>0.2</sub> PW <sub>12</sub> O <sub>40</sub>	58	793
2.5%Au-2.5%Pd/C (2% HNO <sub>3</sub> )	4	746

**Reaction Conditions:** As stated in Table 1.2.

In conclusion, the use of heteropolyacid based catalysts have been shown to be an effective for the direct synthesis of H<sub>2</sub>O<sub>2</sub> under conditions that are attractive to industry. However, much research is still required in this area if these catalysts are to become mainstream in the direct synthesis route and lead to a viable alternative to the indirect auto-oxidation process.

## 1.12. The ammoximation of cyclohexanone to cyclohexanone oxime, utilising TS-1.

Titanium silicate-1 (TS-1) has widely been reported to offer high selectivity and efficiency in oxidation reactions alongside H<sub>2</sub>O<sub>2</sub>, such as aromatic hydroxylation<sup>109, 110</sup>, alkane oxidation<sup>111-113</sup>, and alkene epoxidation,<sup>114,115</sup> with the catalytic conversion of propylene to propylene oxide a key industrial process, with over 1.2 Mt of propylene oxide produced annually.<sup>116</sup> Figure 1.18 highlights the versatility of TS-1 in a range of oxidation reactions when utilised alongside H<sub>2</sub>O<sub>2</sub>.



**Figure 1.18.** Schematic representation of oxidation reactions catalysed by TS-1.<sup>117</sup>

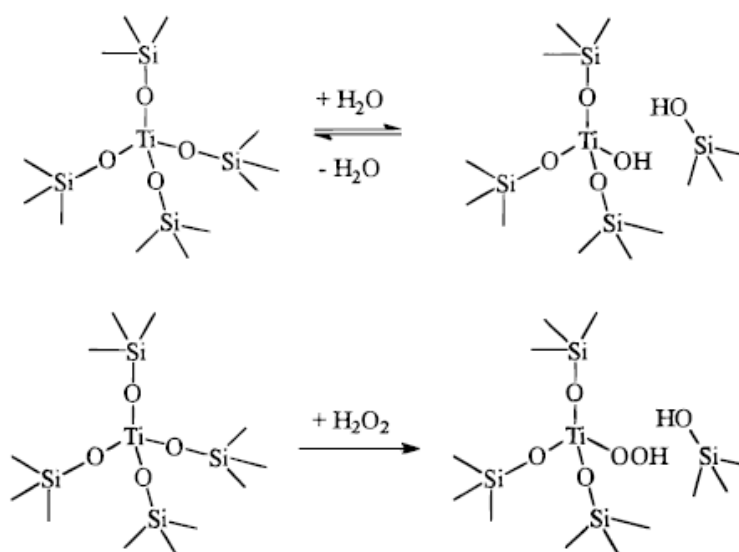
### 1.13. The structure of TS-1.

Analysis of the structure of TS-1 by Drago and co-workers<sup>118</sup> has revealed the absence of strongly acidic sites on TS-1, in comparison to the zeolite HZSM-5, which they have ascribed as the reason for a lack of epoxide ring opening and the utility of TS-1 in epoxidation reactions. TS-1 has an MFI structure formed by three-dimensional systems of channels with dimensions of 0.53 x 0.56 nm and 0.51 x 0.51 nm. The structure of TS-1 prevents all molecules that have a cross-sectional area greater than 0.55 nm diffusing inside the pore structure of the zeolite, affording TS-1 remarkable shape selectivity. For example Hayashi and co-workers<sup>119</sup> have shown that the oxidation of 2-propanol over TS-1 can be strongly retarded by the presence of one molar equivalent of 1-propanol, the linear alcohol is able to coordinate more strongly to the active site, followed by slow oxidation. In comparison the branched alcohol diffuses much slower but undergoes quicker oxidation.

The activity of TS-1 for has been closely related to morphology of the material. For example higher performance towards phenol hydroxylation has been observed for smaller crystals. These smaller crystals are reported to have greater Ti content within the lattice.<sup>115</sup>

The zeolite contains 1 wt % Ti, where the Ti(IV) atoms are incorporated into the framework in tetrahedral sites, substituting some non-adjacent Si atoms. Indeed the active sites for oxidation have been assigned to these isolated, tetrahedral Ti(IV) sites present in an –Si-O-Ti-O-Si- silica matrix, which does not contain Ti-O-Ti bonds. When H<sub>2</sub>O<sub>2</sub> is present at low

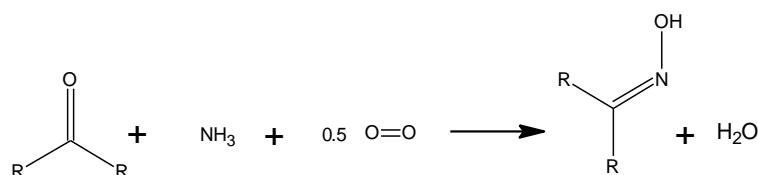
temperatures solvolysis results in the formation of Ti-OOH and Si-OH, as seen in Figure 1.19, with the former giving rise to the active site responsible for catalytic oxidation.<sup>120</sup> The work by Limtrakul and co-workers<sup>121</sup> supports these findings. They demonstrated that formation of hydroxylamine, the key step in the formation of cyclohexanone oxime, discussed in greater detail below, can be divided into two steps; firstly the decomposition of H<sub>2</sub>O<sub>2</sub> over Ti sites to produce a peroxo-titanium species followed by the oxidation of NH<sub>3</sub>. Interestingly their findings suggest that the decomposition of H<sub>2</sub>O<sub>2</sub> occurs primarily on defective Ti sites.<sup>121</sup>



**Figure 1.19.** The formation of the catalytic sites responsible for the formation of hydroxylamine on TS-1.<sup>118</sup>

#### 1.14. The ammoximation of cyclohexanone to cyclohexanone oxime.

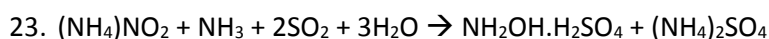
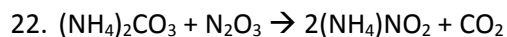
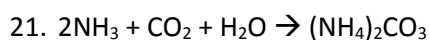
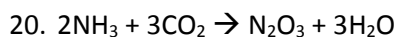
The term ‘ammoximation’ describes the formation of an oxime through reaction of a ketone with ammonia and an oxidant, such as H<sub>2</sub>O<sub>2</sub> or molecular oxygen. As exemplified in Figure 1.20.



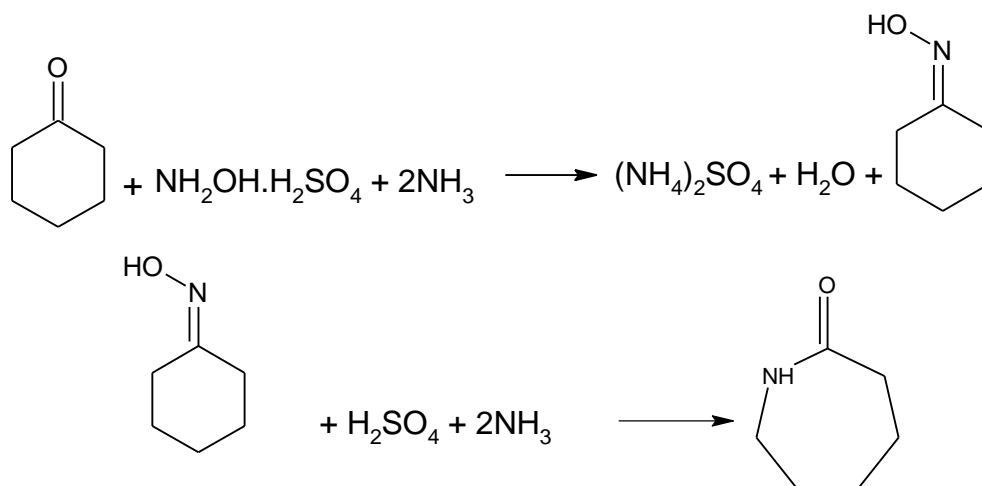
**Figure 1.20.** The conversion of a ketone to an oxime, through reaction with ammonia and oxygen.

The ammoximation reaction may be utilised to form a variety of oximes;<sup>122-124</sup> acetone,<sup>125</sup> butanone,<sup>117</sup> C<sub>5</sub>-C<sub>8</sub> cyclic ketones<sup>117</sup> as well as methyl- and dimethyl- substituted cyclohexanones<sup>126</sup> all yield the corresponding oxime. A key reaction that utilises ammoximation chemistry is the formation of cyclohexanone oxime, from cyclohexanone, a key precursor in the industrial production of ε-caprolactam the monomer of Nylon-6. As of 2010 worldwide production of ε-caprolactam is estimated at approximately 4 Mt / year, with the vast majority (approximately 70 %) utilised in the production of Nylon-6 and the remaining 30 % used in resins and films. In particular demand for Nylon resins has increased in recent years due to its growing use in the automotive industry as well as film-packaging for food and its use in electrical cables.

The industrial formation of ε-caprolactam has been dominated by the Raschig process, where cyclohexanone oxime is formed from cyclohexanone through use of hydroxylamine sulphate, this can then undergo Beckmann rearrangement to form ε-caprolactam. The formation of the hydroxylamine sulphate intermediate is carried out from combination of NH<sub>3</sub>, CO<sub>2</sub> and SO<sub>2</sub> as outlined in Equations 20-23.



The formation of hydroxylamine sulphate results in the formation of a variety of undesired by-products including ammonium sulphate and NO<sub>x</sub>. In particular the environmental issues associated with NO<sub>x</sub> and sulphur oxide formation and co-formation of ammonium sulphate represents significant drawbacks to this process. Furthermore the formation of cyclohexanone oxime, utilising hydroxylamine sulphate, and the successive formation of ε-caprolactam by Beckmann rearrangement also result in the formation of ammonium sulphate, as can be seen in Figure 1.21.

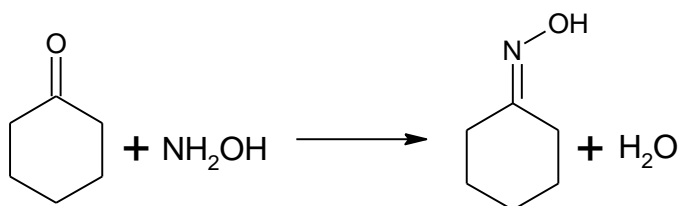


**Figure 1.21.** The formation of caprolactam from cyclohexanone oxime.

The formation of ammonium sulphate, in addition to NO<sub>x</sub>, on a large scale is particularly unattractive, the commercial value of this by-product has declined rapidly in recent years and when coupled with the increasing legislation against NO<sub>x</sub> production an alternative to the Raschig process is of great interest.

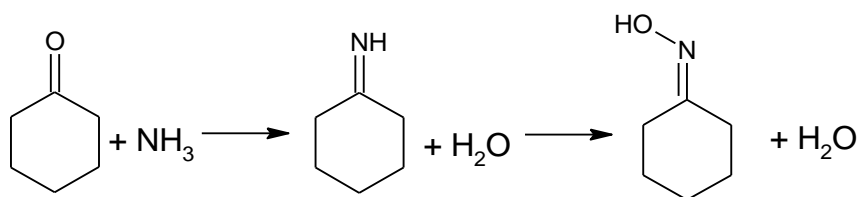
The use of TS-1 for the ammoxidation of cyclohexanone represented a breakthrough in the ammoxidation of cyclohexanone, when it was first reported in 1987 by Roffia and co-workers<sup>127</sup> and since then much interest has grown in the use of TS-1 as catalyst for the formation of cyclohexanone oxime and much research into utilising TS-1 as a catalyst for cyclohexanone ammoxidation has been conducted, with extremely high selectivity towards the oxime and conversion of cyclohexanone achieved.<sup>123, 128-131</sup>

There have been two main mechanistic hypotheses proposed; the iminic route, widely accepted to occur in the gaseous phase, while in the liquid phase general consensus is now behind the hydroxylamine route, discussed below. The hydroxylamine route, shown in Figure 1.22, involves the formation of hydroxylamine via reaction between H<sub>2</sub>O<sub>2</sub> and NH<sub>3</sub> on titanium centers, the basis of this hypothesis is the ability of TS-1 to catalyse the ammoxidation of ketones too large to enter inside the pores and on the ability of TS-1 to generate the hydroxylamine intermediate from NH<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> in the liquid phase. It has been reported by Dal Pozzo and co-workers<sup>132</sup> that the formation of cyclohexanone oxime proceeds via the hydroxylamine route, in the liquid phase.



**Figure 1.22.** Schematic representation of the hydroxylamine route to cyclohexanone oxime formation.

As stated above the formation of cyclohexanone oxime in the gaseous phase is widely reported to proceed via the iminic route.<sup>124,133,134</sup> Firstly the cyclohexanone reacts with NH<sub>3</sub> to form an unstable imine intermediate, which then adsorbs onto the catalyst surface to undergo oxidation to produce the oxime. In this case the role of Ti(IV) is to activate the oxygen, which then inserts into the imine. Figure 1.23 is a schematic representation of the iminic route to cyclohexanone oxime formation.



**Figure 1.23.** Schematic representation of the iminic route to cyclohexanone oxime formation.

Interestingly, recent work by Sooknoi<sup>135</sup> has shown that when acetic acid is used as the solvent the formation of cyclohexanone oxime tends to proceed through the oxidation of the imine, where the imine is formed through the condensation of cyclohexanone with NH<sub>3</sub>. This suggests that the solvent system can influence the route by which the ammoximation reaction proceeds. Interestingly they also report that, again, when acetic acid is used as the solvent it is possible to use a range of ammonium salts as the source of nitrogen. In particular ammonium acetate has been observed to provide a slightly greater yield of oxime when used as the source of nitrogen, in comparison to using ammonia solution.<sup>135</sup>

However the use of TS-1 as a catalyst for the ammoximation of cyclohexanone does have some issues associated. Primarily the presence of high quantities of base results in the leaching of Ti from the zeolite framework. The Ti atoms removed from the framework accumulate on the remaining solid as a non-active hexacoordinated titanium species.<sup>136</sup> This is in stark comparison to the stability observed when TS-1 is utilised in a number of other



oxidation reactions. Activity of the catalyst trends with this loss of Ti from the framework and approaches that of supported Ti. Further issues with catalyst activity are also reported, with deactivation through coke-deposition and a decrease in adsorption capacity with increasing time on-stream reported.<sup>137</sup>

The use of organic solvents such as methanol, toluene and t-butanol to improve catalyst stability have been investigated<sup>128</sup> and all have shown a remarkable ability to retard the loss of crystallinity in TS-1 when subjected to the presence of ammonia, in particular t-butanol is reported to provide the greatest stabilising effect, while also improving catalyst selectivity in comparison to methanol and toluene. However a variety of other solvents for this reaction has been investigated, including acetic acid and water.<sup>135</sup>

### 1.15. Thesis Aims.

The aims of this thesis are outlined below:

1. It has been shown that the use of an acidic reaction medium may lead to an improvement in  $\text{H}_2\text{O}_2$  yield and furthermore acidic supports can improve catalyst selectivity towards  $\text{H}_2\text{O}_2$  synthesis. However, the use of high concentrations of acid can lead to reactor corrosion and the associated increase in maintenance costs and reactor downtime would be of significant concern to industry. While the use of ion exchanged tungstophosphoric acid, a Keggin-type heteropolyacid, as a support for precious metals active towards  $\text{H}_2\text{O}_2$  synthesis reported within the literature. Investigation into the use of Cs-exchanged tungstophosphoric acid as an additive for catalyst known to be active towards the direct synthesis of  $\text{H}_2\text{O}_2$  will be carried out with the aim of improving catalytic activity towards the direct synthesis process and in turn overall yield of  $\text{H}_2\text{O}_2$ .
2. The use of  $\text{H}_2\text{O}_2$ , as an oxidant, alongside TS-1, for the formation of cyclohexanone oxime, via the ammoximation of cyclohexanone has been investigated thoroughly in the literature. However the addition of  $\text{H}_2\text{O}_2$  to the reaction mixture requires the concentration, transportation, storage and subsequent dilution of  $\text{H}_2\text{O}_2$ . All of which result in additional costs and have some significant risk attached. The *in-situ* formation of  $\text{H}_2\text{O}_2$  and subsequent utilisation in the ammoximation of cyclohexanone, in a one pot approach, would offset many of these unwanted expenses and will be studied within this thesis.

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## 2. Experimental

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This Chapter outlines the experimental procedures followed during catalytic preparation, testing and material characterisation discussed in this Thesis.

### 2.1. Materials used

This Section outlines the chemicals used during the work contained within this thesis and the suppliers used with the purity of the various chemicals in parenthesis.

PdCl<sub>2</sub> – Johnson Matthey (99.99% trace metal basis)

HAuCl<sub>4</sub> - Johnson Matthey (99.99% trace metal basis)

H<sub>2</sub>PtCl<sub>6</sub> - Johnson Matthey (99.99% trace metal basis)

Tungstophosphoric acid hydrate Sigma Aldrich (99.995 % trace metal basis)

CsNO<sub>3</sub> – Sigma Aldrich (99.99 % trace metal basis)

TS-1 – ACS Materials (≥ 99.0 %)

TiO<sub>2</sub> – Degussa p25 (99.5 % trace metal basis, 20-30 nm particle size)

SiO<sub>2</sub> – Fischer Scientific (60 A Particle size 35 – 70 micron, Silice 60A)

Carbon G60 – Sigma Aldrich (Darco powder – 100 mesh particle size)

MeOH – Sigma Aldrich (HPLC Grade)

EtOH - Sigma Aldrich (HPLC Grade)

t-BuOH - Sigma Aldrich (≥ 99.0 %)

Diethylene glycol monoethyl ether – Sigma Aldrich (≥99.0%)

Water – Fischer Scientific (HPLC Grade)

50 % H<sub>2</sub>O<sub>2</sub> - Sigma Aldrich (Stabilised)

35 % H<sub>2</sub>O<sub>2</sub> - Sigma Aldrich (Stabilised)

Cyclohexanone - Sigma Aldrich (99.8%)

Cyclohexanone oxime - Sigma Aldrich (97%)

28% NH<sub>3</sub> in water – Sigma Aldrich (≥ 99.99 % trace metals)

Ce(SO<sub>4</sub>)<sub>2</sub> Sigma Aldrich (> 98 %)

(NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O - Sigma Aldrich (> 98%)

## 2.2. Catalyst Preparation

### 2.2.1. Gold, Palladium and Gold-Palladium Catalysts prepared by wet impregnation.

Monometallic and bi-metallic gold, palladium catalysts were prepared by wet impregnation and co-impregnation of the appropriate support with solutions of  $\text{HAuCl}_4$ ,  $\text{PdCl}_2$ , using an excess of solvent (in this case water). The catalysts were prepared to have a nominal metal content of 5 wt. %, unless otherwise stated.

A typical 1.0 g preparation procedure of a 2.5 wt. % Au- 2.5 wt. % Pd / support catalyst was carried out according to the following procedure which has been previously reported in the literature<sup>1</sup>.

0.042 g of  $\text{PdCl}_2$  was added to 2.04 ml of  $\text{HAuCl}_4$  (12.25 g Au / 1000 ml) and heated to 80 °C with stirring and left until the  $\text{PdCl}_2$  had completely dissolved. 0.95 g of the desired support was then added to the solution and the water allowed to evaporate until the mixture formed a paste like consistency. The samples were dried at 110 °C for 16 h and then calcined in static air at 400 °C for 3 h with a ramp rate of 20 °C min<sup>-1</sup>.

### 2.2.2. Gold, Palladium, Platinum and Gold - Palladium - Platinum Catalysts prepared by wet impregnation.

Tri-metallic Au-Pd-Pt catalysts were prepared in a similar manner to Au-Pd catalysts, discussed in Section 2.2.1. The procedure for producing 1 g of 2 wt. % Au – 2 wt. % Pd -1 wt. % Pt supported catalyst is outlined below:

0.033 g of  $\text{PdCl}_2$  was added to 1.63 ml of  $\text{HAuCl}_4$  (12.25 g Au / 1000 ml) and 1 ml of  $\text{H}_2\text{PtCl}_6$  (10 g Pt / 1000 ml) and heated to 80 °C with stirring and left until the  $\text{PdCl}_2$  had completely dissolved. 0.95 g of the desired support was then added to the solution and the water allowed to evaporate until the mixture formed a paste like consistency. The samples were dried at 110 °C for 16 h and then calcined in static air at 400 °C for 3 h with a ramp rate of 20 °C min<sup>-1</sup>.

### 2.2.3. Cs-exchanged tungstophosphoric acid.

The degree of Cs-incorporation into the structure of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  was varied by varying the mass of  $\text{CsNO}_3$  added to an aqueous solution of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . A typical 1.0 g preparation



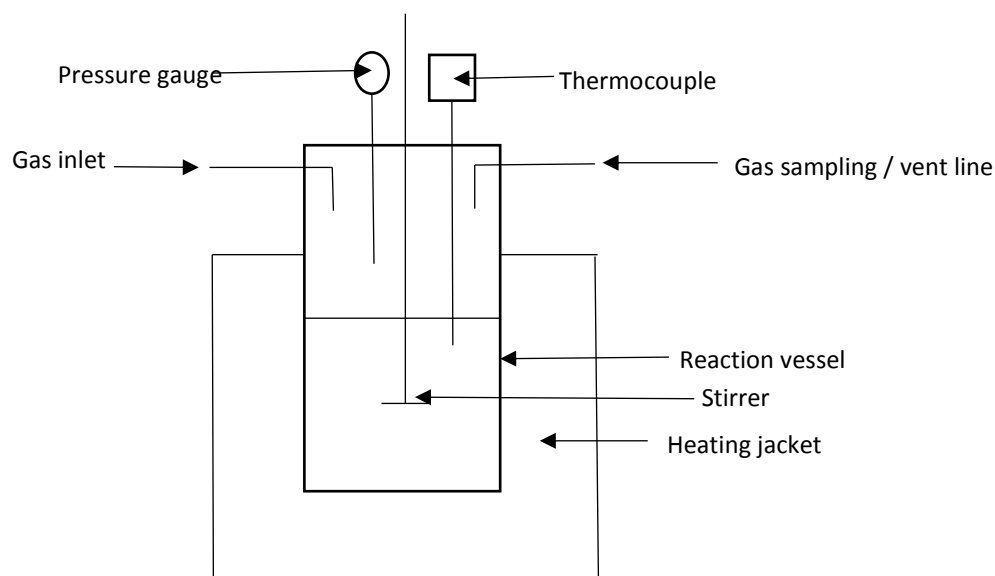
procedure of  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  was carried out according to the following procedure which has been previously reported in the literature<sup>2</sup>.

$\text{CsNO}_3$  (0.151 g) dissolved in 5.0 ml deionised water was added drop-wise to an aqueous solution of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (0.892 g) while stirring. The resulting solution was continuously stirred while heating (80°C). The water was allowed to evaporate until the mixture formed a paste like consistency. The samples were dried at 110 °C for 16 h and then calcined in static air at typically 300 °C for 2 h with a ramp rate of 20 °C min<sup>-1</sup>.

## 2.3. Catalyst Testing

### 2.3.1. The Direct Synthesis of $\text{H}_2\text{O}_2$ .

Catalytic activity towards the direct synthesis of  $\text{H}_2\text{O}_2$  from  $\text{H}_2$  and  $\text{O}_2$  was determined using a Parr Instruments stainless-steel autoclave (equipped with overhead stirrer and temperature/pressure sensors) with a nominal volume of 100 ml and maximum working pressure of 14 MPa, as shown in Figure 2.1 below. During a standard synthesis reaction the autoclave was charged with MeOH (5.6 g), HPLC standard  $\text{H}_2\text{O}$  (2.9 g) and catalyst (0.01 g). The autoclave was pressurised with 2.9 MPa 5 %  $\text{H}_2$  /  $\text{CO}_2$  and 1.1 MPa 25 %  $\text{O}_2$  /  $\text{CO}_2$  to give a total reaction pressure of 4 MPa. After cooling the autoclave to 2 °C (or reaching the given temperature) the reaction mixture is stirred at 1200 rpm for 0.5 h. The reaction starts when stirring begins, if stirring does not occur no  $\text{H}_2\text{O}_2$  is observed, over the timescale of the reaction. After the reaction was completed a gaseous sample was collected and analysed by gas chromatography (discussed in Section 2.4.1) when necessary. After collection of the gaseous sample the remaining reactant gas was vented and the catalyst was removed from the solvent by filtration and two 0.5 g aliquots of the solvent were titrated against a  $\text{Ce}(\text{SO}_4)_2$  solution acidified with 2%  $\text{H}_2\text{SO}_4$  using ferroin as an indicator. The concentration of the  $\text{Ce}(\text{SO}_4)_2$  solution was determined by titration of a known amount of  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , using ferroin as an indicator.<sup>1</sup>



**Figure 2.1.** Schematic representation of a high pressure autoclave.

Catalytic performance was compared by determining the average rate of  $\text{H}_2\text{O}_2$  formation, normalised for catalyst mass, to give a productivity value which is reported a  $\text{mol}_{\text{H}_2\text{O}_2}\text{h}^{-1}\text{kg}_{\text{cat}}^{-1}$ . The wt. % of  $\text{H}_2\text{O}_2$  was also determined using the equations shown below:

$$\text{Ce}(\text{SO}_4)_2 \text{ to titrate whole reaction solution} = \frac{\text{Titre} \times 8.5 (\text{total solution volume})}{\text{Sample mass}}$$

$$\text{Moles Ce}(\text{SO}_4)_2 = \frac{\text{Vol. of Ce}(\text{SO}_4)_2 \text{ to titrate whole reaction solution} \times [\text{Ce}(\text{SO}_4)_2]}{1000}$$

$$\text{Moles H}_2\text{O}_2 = \frac{\text{Moles Ce}(\text{SO}_4)_2}{2}$$

$$\text{Productivity} = \frac{\text{Moles H}_2\text{O}_2}{\text{Catalyst Mass (Kg)} \times \text{Reaction Time (h)}}$$

$$\text{wt \% H}_2\text{O}_2 = \frac{\text{Moles H}_2\text{O}_2 \times \text{Molecular Mass H}_2\text{O}_2}{8.5 (\text{total mass of solvent})}$$

### 2.3.2. Degradation of H<sub>2</sub>O<sub>2</sub>.

The degradation activity of a catalyst towards H<sub>2</sub>O<sub>2</sub> was determined in a manner similar to the direct synthesis activity of a catalyst. The autoclave was charged with MeOH (5.6 g), H<sub>2</sub>O<sub>2</sub> (50 wt. % 0.69 g) HPLC standard H<sub>2</sub>O (2.21 g) and catalyst (0.01 g). The solvent composition is equivalent to a 4 wt. % H<sub>2</sub>O<sub>2</sub> solution; this allows for comparison to previous work conducted within the Hutchings's research group. It is a larger concentration than that which can be produced in a standard synthesis reaction (outlined in Section 2.3.1 above) and allows for accurate determination of catalyst activity towards degradation. From the solution two aliquots were removed by pipette of between 0.04 g and 0.06 g +/- 1mg were removed and titrated with acidified Ce(SO<sub>4</sub>)<sub>2</sub> solution using ferroin as an indicator to determine an accurate concentration of H<sub>2</sub>O<sub>2</sub> at the start of the reaction. The autoclave was pressurised with 2.9 MPa 5 % H<sub>2</sub> / CO<sub>2</sub> and cooled to 2 °C, unless otherwise stated, and the reaction mixture was stirred at 1200 rpm for 0.5 h. The reaction starts when stirring begins, if stirring does not occur no H<sub>2</sub>O<sub>2</sub> degradation is observed, over the timescale of the reaction. After the reaction was complete (0.5 h) the catalyst was immediately removed from the reaction solvents and as previously two aliquots of 0.05 g were titrated against the acidified Ce(SO<sub>4</sub>)<sub>2</sub> solution using ferroin as an indicator. The degradation activity was calculated as mol<sub>H<sub>2</sub>O<sub>2</sub></sub> h<sup>-1</sup> kg<sub>cat</sub><sup>-1</sup> along with the percentage of H<sub>2</sub>O<sub>2</sub> remaining after the reaction.

A 'blank' degradation test was carried out routinely to determine the contribution of the reactor to the degradation of H<sub>2</sub>O<sub>2</sub>. This followed the same procedure as that described in Section 2.3.2, however no catalyst was included. If any H<sub>2</sub>O<sub>2</sub> degradation was observed the reactor was cleaned with aqua regia, to remove any metal deposited on the reactor vessel, followed by thorough cleaning with water. Once this was complete a second 'blank' reaction was carried out to ensure all deposited metal had been removed.

### 2.3.3. Direct synthesis of H<sub>2</sub>O<sub>2</sub> under ammoximation conditions.

Catalytic activity towards H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> was determined under conditions approaching those used in the ammoximation process. A standard synthesis reaction, as outlined in Section 2.3.1. is carried out where MeOH is replaced by t-BuOH and a known volume of H<sub>2</sub>O is replaced by cyclohexanone and /or NH<sub>3</sub>, to ensure total volume remains constant. The choice of t-BuOH as a solvent stems from its use in literature investigating the ammoximation of cyclohexanone and this is discussed in greater detail in Chapter 1. Once the reaction was completed a gas sample undergoes analysis by gas chromatography to determine H<sub>2</sub>

selectivity prior to analysing a liquid sample, for cyclohexanone conversion and cyclohexanone oxime selectivity, also by gas chromatography.

#### 2.3.4. Degradation of H<sub>2</sub>O<sub>2</sub> under ammoximation conditions.

The degradation activity of a catalyst towards H<sub>2</sub>O<sub>2</sub> was determined in a manner similar to that described above in Section 2.3.2. However unlike above the autoclave was charged with t-BuOH (5.6 g), H<sub>2</sub>O<sub>2</sub> (50 wt. % 2.07 g) HPLC standard H<sub>2</sub>O (0.83 g) and catalyst (0.01 g). The solvent composition is equivalent to a 12 wt. % H<sub>2</sub>O<sub>2</sub> solution. The higher concentration of H<sub>2</sub>O<sub>2</sub> is required as the conditions utilised for the ammoximation of cyclohexanone are quite harsh and a smaller concentration would not allow for accurate determination of the contribution of the reaction conditions and the catalyst towards the degradation of H<sub>2</sub>O<sub>2</sub>.

#### 2.3.5. The ammoximation of cyclohexanone to cyclohexanone oxime via H<sub>2</sub>O<sub>2</sub> addition.

To determine the effect of metal impregnation on catalytic ability to produce cyclohexanone oxime the following procedure was followed:

Cyclohexanone (1.0 g, 10 mmol), catalyst (0.05 g), t-BuOH (2.5 g), H<sub>2</sub>O (2.5 g) and 28 wt. % NH<sub>3</sub> (12 mmol, 0.73 g) were added into a two neck flask with condenser attached. The second flask neck is equipped with a H<sub>2</sub>O<sub>2</sub> inlet line. The reaction mixture was heated, with stirring, to 80 °C and H<sub>2</sub>O<sub>2</sub> (35 wt. %, 10 mmol, 0.89 g) was added over 1 h using a HPLC pump, at a rate of 0.0148 mlmin<sup>-1</sup>. The reaction was allowed to continue for a further 0.5 h. After this time the reaction mixture was allowed to cool to room temperature and ethanol (10 ml) and internal standard (diethylene glycol monoethyl ether) (1.0 g) are added. The catalyst is removed by filtration and the mixture is analysed by gas chromatography.

#### 2.3.6. Catalyst re-use for the ammoximation of cyclohexanone to cyclohexanone oxime via H<sub>2</sub>O<sub>2</sub> addition.

Catalyst reusability was tested by running an ammoximation as outlined in Section 2.3.5 but increasing the catalyst mass to 0.1 g and using twice the standard reactant amounts. The addition rate of H<sub>2</sub>O<sub>2</sub> (35 wt. %) was set to 0.297 mlmin<sup>-1</sup>. After the reaction was complete the catalyst was removed by filtration and was allowed to dry at 110 °C for 16 h on the filter paper to ensure the sample was completely dry. Following this procedure an ammoximation test as described in Section 2.3.5 was conducted.

### 2.3.7. The ammoximation of cyclohexanone to cyclohexanone oxime via *in-situ* synthesis of $\text{H}_2\text{O}_2$ .

Catalytic performance for the *in-situ* ammoximation of cyclohexanone was determined using a Parr Instruments stainless-steel autoclave (equipped with overhead stirrer and temperature/pressure sensors) with a nominal volume of 50 ml and maximum working pressure of 14 MPa. During a standard ammoximation reaction the autoclave was charged with cyclohexanone (0.13 g, 1.3 mmol), catalyst (0.05 g), *t*-BuOH (5.6 g),  $\text{H}_2\text{O}$  (2.69 g) and 28 wt. %  $\text{NH}_3$  (0.08 g, 1.3 mmol). The autoclave was pressurised with 2.9 MPa 5 %  $\text{H}_2$  /  $\text{CO}_2$  and 1.1MPa 25 %  $\text{O}_2$  /  $\text{CO}_2$  to give a total reaction pressure of 4 MPa. The autoclave was then heated to the desired temperature and stirred at 1200 rpm for 1.5h.

After the reaction was complete, and the autoclave allowed to cool to room temperature, a gas sample was taken for analysis by GC. Following this, ethanol (1 ml) and internal standard (diethylene glycol monoethyl ether) (0.1 g) were added to the working solution. The catalyst was removed by filtration and the mixture was analysed by gas chromatography.

### 2.3.8. Hot filtration for the ammoximation of cyclohexanone to cyclohexanone oxime via *in-situ* synthesis of $\text{H}_2\text{O}_2$ .

In order to establish the activity of leached metal towards the ammoximation of cyclohexanone a hot filtration test was carried out. This involves running a standard reaction, as outlined in Section 2.3.7. After the reaction was complete, and the autoclave allowed to cool to room temperature, a gas sample was taken for analysis. Following this the catalyst was removed by filtration and the reaction solution returned to the reactor which was pressurised with 2.9 MPa 5 %  $\text{H}_2$  /  $\text{CO}_2$  and 1.1MPa 25 %  $\text{O}_2$  /  $\text{CO}_2$  to give a total reaction pressure of 4 MPa. The autoclave was then heated to the desired temperature and stirred at 1200 rpm for 0.5 h.

After the reaction was complete analysis of both the reaction solution and reactant gas carried out, as outlined above in Section 2.3.7.

## 2.4. Gas Chromatography.

### 2.4.1. GC setup for analysis of gas from H<sub>2</sub>O<sub>2</sub> direct synthesis reaction.

A Varian 3800 gas chromatogram fitted with a thermal conductivity detector was used to analyse the post reaction gas mixture from the direct synthesis reaction. In order to determine catalytic conversion of H<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> selectivity a gas sample from a 'blank' direct synthesis reaction (where no catalyst is present, but all other conditions are the same as those outlined above) is analysed by GC. This is to allow comparison of the gas composition after the catalysed direct synthesis reactions and calculation of H<sub>2</sub> conversion and H<sub>2</sub>O<sub>2</sub> selectivity.

The column oven (containing a Porapak Q column) was held at 30 °C for 22 min which allows separation of H<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub>, using Argon as a carrier gas at a flow rate of 30 ml / min. The retention times of the components analysed during a H<sub>2</sub>O<sub>2</sub> synthesis reaction is shown in Table 2.1.

**Table 2.1.** Retention times of components analysed during the direct synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub>.

Component	Retention time / min
H <sub>2</sub>	1.63
O <sub>2</sub>	2.24
CO <sub>2</sub>	9.21

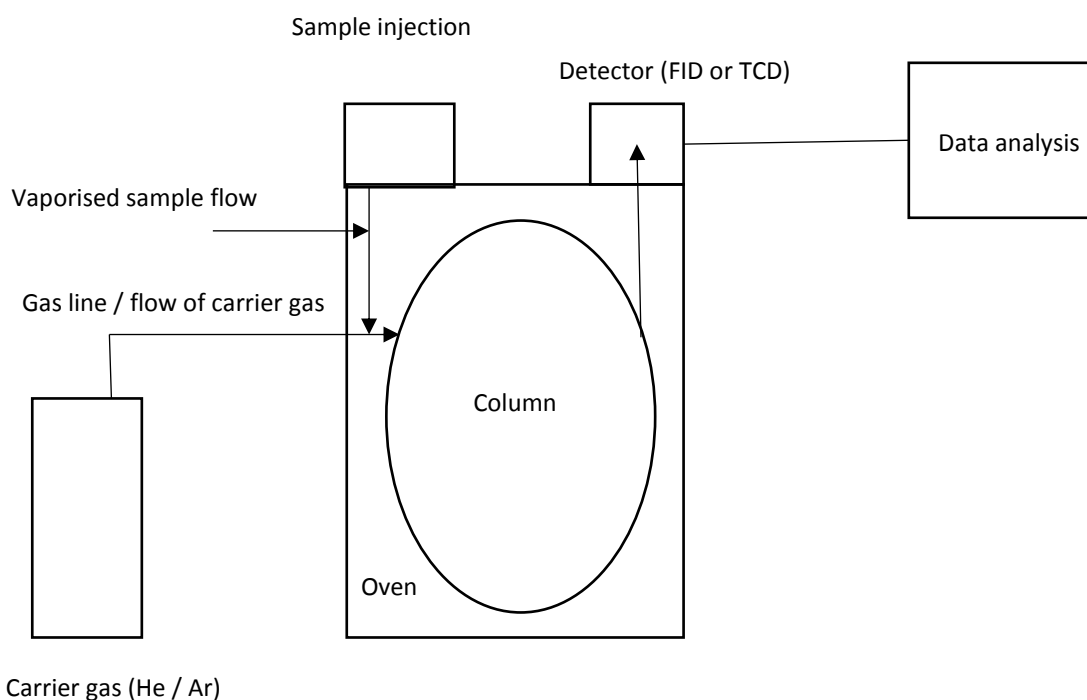
Hydrogen conversion was measured by calculating the difference between H<sub>2</sub>: CO<sub>2</sub> ratio before and after the reaction. H<sub>2</sub> selectivity was calculated based on the rate of H<sub>2</sub>O<sub>2</sub> synthesised at the end of the direct synthesis reaction.

### 2.4.2. GC set up for analysis of reaction mixture from ammoximation of cyclohexanone.

A Varian 3800 gas chromatogram fitted with a flame ionisation detector was used to analyse the reaction mixture of the cyclohexanone ammoximation process post reaction. In order to provide quantitative analysis of the reaction mixture, samples containing known concentrations of reactant, products, solvent and standard are first used to establish retention factors and allow the conversion of cyclohexanone, selectivity toward cyclohexanone oxime and overall yield to be calculated.

The column oven (containing a CP – Wax 52 CB column, with a polyethylene phase) temperature was held at 80 °C for 1 minute upon injection of the liquid sample. Secondly temperature was increased from 80 °C to 200 °C, at a ramp rate of 15 °C / min for a total ‘run time’ of 9 minutes. This allows for the elution of the analytes within the gaseous sample. Following from this the temperature is raised to 250 °C, at a ramp rate of 20 °C / min, this temperature is held for five minutes and ensures that no sample remains within the column, which may affect subsequent analysis.

Column pressure was maintained at 5 psi and the FID temperature was set to 270 °C. A carrier gas of He was utilised and a flow rate of 10 ml/min was chosen. In order to maintain sensitivity a splitless injection was utilised; the role of split injections is discussed below.



**Figure 2.2.** Schematic representation of a Gas Chromatograph.

Gas chromatography is a technique used to separate and analyse mixtures of chemical compounds, either liquid or gaseous. Liquid samples are first vaporised by an injector block, often set to a temperature higher than that of the column oven. Elution is brought about by a flowing of an inert gas for example He or N<sub>2</sub> termed the mobile phase. The mobile phase carries the vaporised sample through the column and does not interact with the analyte.

The stationary phase is an adsorbent or a high boiling point liquid on an inert material known as the stationary support, commonly used supports are diatomaceous earth, silica gel or alumina. The stationary phase is usually held in glass, quartz or stainless steel tubes.

There are generally two types of column: packed and capillary columns. These are enclosed in a thermostatically controlled oven, the temperature of which can range from ambient to over 400 °C and can remain constant during a separation or increase at a determined rate to increase elution.

There are a number of techniques for introducing the sample onto the column; split injection limits the amount of sample (approximately 2 %) allowed to pass onto the column and this can present issues with sensitivity. The splitting ratio can be altered using resistance to liquid sample flow. While a splitless injection overcomes this disadvantage.

There are many detectors available to monitor the carrier gas as it emerges from the column and act in response to changes in the gas composition as analytes are eluted. One of the most commonly used detectors is the Flame Ionisation Detector (FID). The effluent gas, once passed through the column is mixed with H<sub>2</sub> and air and is burned at a small metal jet. The jet forms the anode of an electrolytic cell and the cathode or collector anode is placed just above the flame tip. The pyrolysis of organic compounds often leads to the formation of ions and electrons and detection involves monitoring the current produced by the movement of these charge carriers from anode to cathode. The numbers of ions produced by pyrolysis of the organic analytes are proportional to the number of reduced carbon atoms in the flame and so quantitative analysis is possible<sup>3</sup>.

A thermal conductivity detector (TCD) is another common detector used in gas chromatography. The principle of operation is based on the relative change in the thermal conductivity of the gas passing across the detector filament, as the analytes elute from the column. Heat is lost continuously from the filament through the carrier gas to the wall of the detector. Through measuring the current required to maintain the temperature of the filament as the analytes pass over the filament a chromatographic signal is produced.

#### 2.4.3. Quantitative Analysis by Gas Chromatography.

For quantitative analysis of how reactant concentration changes during a reaction ethanol is added to the reaction mixture (to ensure all product is dissolved) and an external standard (Diethylene glycol monoethyl ether) is added to the reaction mixture, post reaction and the catalyst is removed by filtration. A sample of this mixture is then injected into the GC. The

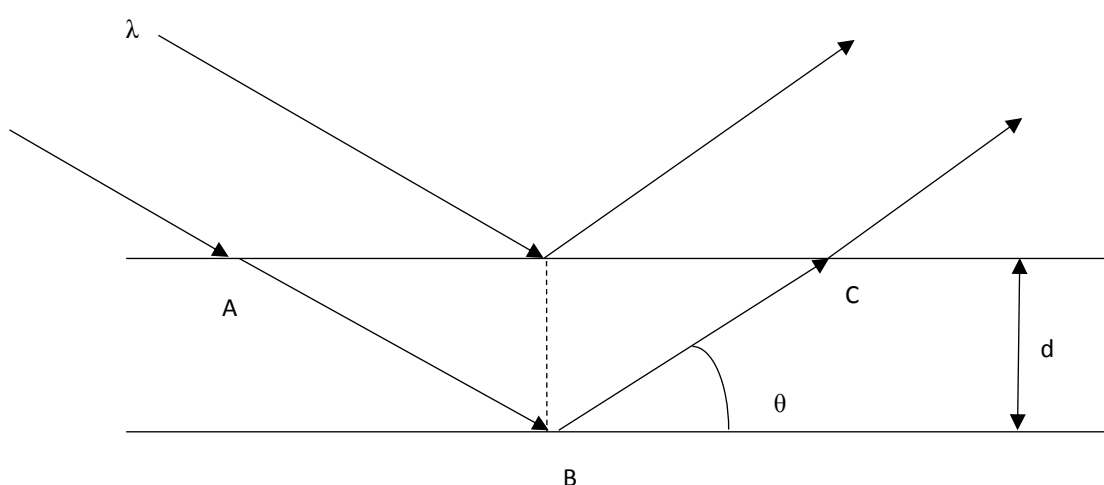


number of moles of reactant were determined from its mass pre-reaction and post reaction concentration is determined from the normalised area of the substrate signal from the FID. Cyclohexanone conversion, selectivity towards cyclohexanone oxime and cyclohexanone oxime yield are then calculated using the equations found in Appendix 2.1.

## 2.5. X-Ray Diffraction (XRD).

X-ray diffraction (XRD) is a bulk characteristic technique that allows the identification of crystallites and allows the detection of crystallite size greater than  $5\text{nm}^4$ . It is a non-destructive technique with a detection limit of approximately 5 wt%.

X-rays are formed by bombarding a metal target, usually Cu or Mo, with a high energy electrons emitted from a thermionic emission from a filament, usually W or Mo. The filament temperature can be varied in order to regulate generation of electrons. Collision of the incident electrons with the metal target produces a broad range of X-rays from the K-shell (1s) of the target atoms. X-rays are emitted as the resultant vacancies are filled with electrons from the L (2p) or M (3p) levels which have superimposed onto it characteristic narrow energies known as  $K_\alpha$  and  $K_\beta$ . The X-rays produced are filtered to give a monochromatic source and the collision of these monochromatic X-rays with the atomic planes of the crystalline sample results in scattering of the X-rays, this can result in constructive interference (a 'reflection'), when the spacing between lattice planes ( $d$ ) is equal to an integer number of wavelengths or when  $AB + BC = n\lambda$ . Figure 2.3 shows X-ray interaction with lattice planes of a crystalline sample.



**Figure 2.3.** Diagram to show X-ray diffraction from lattice planes within a crystallite, where  $d$  represents lattice spacing and  $\theta$  is the incident angle, normal to the plane.

Powder samples have an infinite number of randomly orientated crystallites, the collision of X-rays with the sample results in the scattering of these X-rays at the appropriate  $2\theta$  angle, as defined by Bragg's Law. It is possible to consider the crystallite as a stack of reflecting lattice planes, with separation between each plane denoted as  $d$ . When two X-rays are reflected by adjacent lattice planes, shown in Figure 2.3 the first X-ray strikes the upper lattice plane at a given point, however the second X-ray travels an additional distance (AB) before striking the second lattice plane. Once reflected by the respective lattice planes the two X-rays will differ in path length by a distance denoted as BC. It is therefore possible to describe the difference in net path length as:

$$AB + BC = 2d \sin \theta$$

For the majority of incident X-rays the incident angle or glancing angle ( $\theta$ ) the path-length difference will not equate to an integer of wavelengths, and these waves interfere destructively. However when the path-length difference is an integer number of the wavelengths the reflected X-rays are in-phase and interfere in a constructive manner and so it is possible to observe a reflection when the incident angle obeys Bragg's Law.

$$n\lambda = 2d \sin \theta$$

Where :

$n$  = an integer,

$\lambda$  = X-ray wavelength,

$d$  = lattice spacing,

$\theta$  = angle between incident and normal to the plane.

Smaller crystallites, such as supported metallic nanoparticles, incomplete destructive interference can result in line broadening. This means that the shape of the reflection can provide information with regard to crystallite size. Larger crystallites, with more lattice planes will produce sharp, narrow peaks, while smaller crystallites will give rise to broader reflections. It is possible to estimate the crystallite size of a supported metallic nanoparticle using the Debye-Scherrer equation, shown below. Although this is limited to particles larger than 5 nm as below this limit the incident X-rays are not scattered to a great enough angle to be measured<sup>5</sup>.

$$n = \frac{k \lambda}{\beta \cos \theta}$$

Where: n = crystallite size

k = form factor,

$\lambda$  = X-ray wavelength,

$\beta$  = full width half maximum of the reflection

$\theta$  = diffraction angle.

Procedure:

Investigation of the bulk structure of the crystalline materials was carried out using a ( $\theta$ - $\theta$ ) PANalytical X'pert Pro powder diffractometer using a Cu K $\alpha$  radiation source, operating at 40 KeV and 40mA. Standard analysis was carried out using a 40 minute run with a back filled sample, between 2 $\theta$  values of 10 – 80°. Phase identification was carried out using the International Centre for Diffraction Data (ICDD).

## 2.6. BET Surface Area Analysis.

The surface area of a powdered material can be determined by physical adsorption of a gas onto the surface of the solid, through weak Van der Waals forces between the adsorbate and the surface of the adsorbent.

The concept builds on Langmuir adsorption theory, which is a theory for monolayer adsorption, based on three assumptions:

1. Adsorption cannot exceed monolayer coverage.
2. The surface of the adsorbent is uniform, with all sites being equivalent.
3. The ability of an adsorbate molecule to adsorb on to a specific site is not dependent on the presence of pre-existing adsorbed molecules on neighbouring sites.

BET theory extends Langmuir theory to multilayer adsorption and assumes that gas molecules can physically adsorb to the surface of the sample infinitely, that there is no interaction between each adsorption layer and finally that Langmuir theory can be applied to each layer of adsorption. According to BET theory the rate of adsorption is equal to the rate of desorption once equilibrium has been reached.

The sample is first pre-treated in order to remove adsorbents, such as water or solvent from the sample surface. Following this physical adsorption of the adsorbate occurs, utilising varying pressures of N<sub>2</sub>. The amount of N<sub>2</sub> adsorption can be related to pressure through the following adsorption isotherm equation.

$$\frac{P}{v(P_0 - P)} = \frac{1}{v_m C} + \frac{C - 1}{v_m C} \frac{P}{P_0}$$

Where:

P = equilibrium constant

P<sub>0</sub> = saturation pressure

v = volume

v<sub>m</sub> = volume required to cover the surface in a monolayer

C = constant

The equation above can be linearised through a plot of  $\frac{P}{v(P_0 - P)}$  versus  $\frac{P}{P_0}$  where the intercept occurs at  $\frac{1}{v_m C}$ .

The surface area can then be determined using the following equation:

$$Surface\ area = \frac{v_m * N_A * S}{M}$$

Where v<sub>m</sub> = volume required to cover the surface in a monolayer

N<sub>A</sub> = Avagadro's Number (6.023x10<sup>23</sup>)

S = cross sectional area of N<sub>2</sub> (0.162 nm<sup>2</sup>)

Procedure:

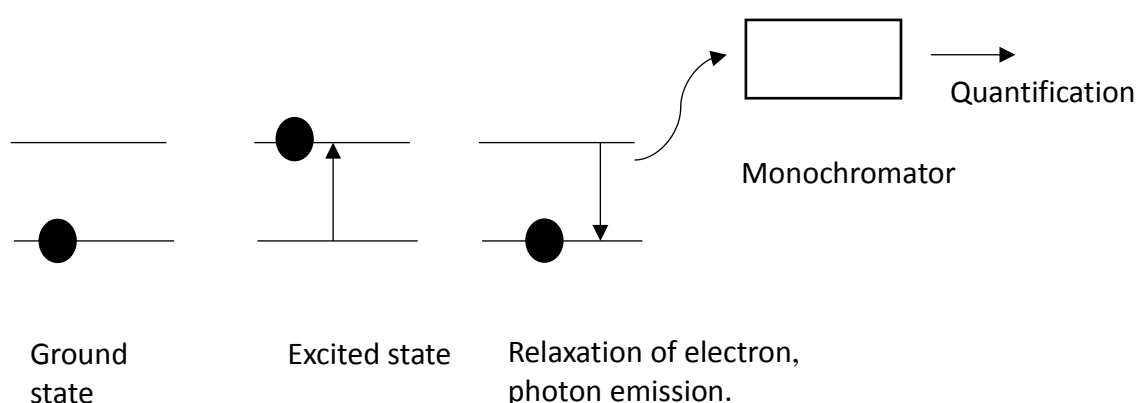
Surface area analysis was determined using a Micromeritics Gemini 2360 analyser. A known amount of sample, 100–200 mg was placed in a straight walled tube and degassed for 1 h at 120°C under a flow of N<sub>2</sub>. The surface area was analysed using a single point analysis typically taking 5 points between P/P<sub>0</sub>= 0.05–0.1.

## 2.7. Microwave Plasma Atomic Emission Spectroscopy (MP-AES).

MP-AES is an elemental analytical technique that is based on the principles of atomic emission. It utilises on a microwave and magnetically excited nitrogen plasma formed within a quartz torch. Samples analysis can range from examination of a reaction solution to determine leaching to digestion of metals from a support to determine accurate loadings. However this limits catalyst samples to those that are soluble or digestible, in comparison inductively coupled plasma (ICP) emission spectroscopy allows for solid analyse samples via laser ablation systems.

The nitrogen plasma is heated approximately 5000 Kelvin and causes atomisation of the sample and leads to the formation of a high population of excited states, providing MP-AES with a high sensitivity in comparison to those techniques which utilise a lower temperature, such as flame absorption spectroscopy.

Figure 2.4 outlines the principles of MP-AES, the uptake of the sample and introduction into the nitrogen plasma leads to excitation of electrons from the ground to the excited state. These electrons then relax to the lower quantised energy level, releasing photons of defined energy and wavelength as they do so. These energies and wavelengths are characteristic to each element and allow the use of a monochromator and mirror grating allows the analysis of individual wavelengths in a sequential manner. This, along with high intensities leads to low interference and a high sensitivity for each element.



**Figure 2.4.** Schematic of basic principles of microwave plasma atomic emission spectroscopy.

Procedure:

Reaction solutions were first filtered to remove heterogeneous catalyst from the sample. Dilution of the sample with low chain alcohol such as ethanol was then conducted in order to avoid issues associated with the use of long chain organics utilised as the reaction medium, this dilution occurred in a 1 : 1 ratio, where 1 ml of ethanol was utilised for 1 ml of sample. Further filtration occurred using PTFE syringe filters (0.456  $\mu\text{m}$ ). Samples were then analysed using an Agilent MP-AES 4100, samples were investigated for the presence of precious metals (Au, Pd and Pt) using multiple wavelength calibrations for each individual element.

## **2.8. Electron Microscopy (EM).**

### **2.8.1. Transmission electron microscopy (TEM).**

Transmission electron microscopy (TEM) is a non-destructive technique that is utilised in heterogeneous catalyst characterisation, in particular it provides information with regards to particle size and dispersion as well as chemical composition, when coupled with Energy-dispersive X-ray spectroscopy (EDX). TEM has an approximate resolution of 5  $\text{\AA}$ <sup>5</sup>.

TEM utilises a high energy and high intensity electron beam, passed through a condenser which excludes high angle electrons to produce parallel rays, which are then impinge on the sample. Beam attenuation is dependent on the density and thickness of the sample under investigation and the transmitted electrons form a two-dimensional projection of the sample mass. As the electrons pass through the sample the electrostatic potential of the constituent elements within the sample cause the electrons to become scattered, subsequent magnification by electron optics lead to the formation of the bright-field image. The dark field image is obtained from the diffracted electron beams, which are slightly off angle from the transmitted beam. The position of the aperture it is possible to choose whether the diffracted beam (dark field) or the un-scattered electrons (bright field) are used to produce the image.

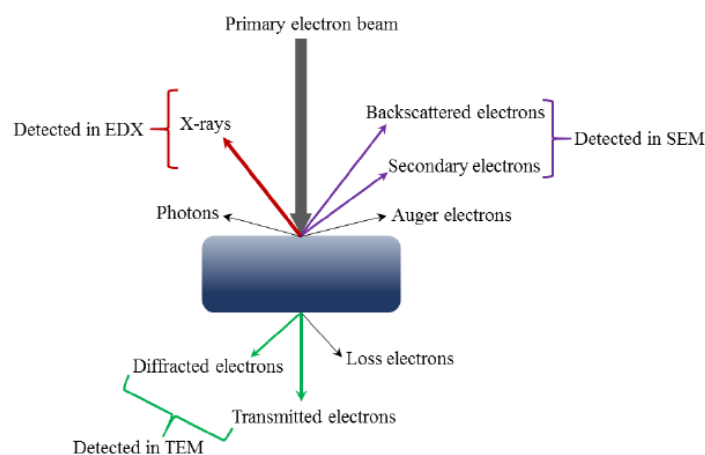
Typical operating procedures are 100-200keV electrons,  $10^{-6}$  mbar vacuum, 0.3 nm resolution and a magnification of  $3 \times 10^5$  to  $10^6$ . In general the identification of supported nanoparticles, such as supported metal nanoparticles requires that there is adequate contrast between the support and the particles themselves and that a thin sample, typically less than 100 nm, is utilised<sup>5</sup>.

### 2.8.2. Scanning Transmission Electron Microscopy (STEM).

STEM operates in a manner very similar to scanning electron microscopy (SEM), it can provide information about particle morphology at the atomic scale<sup>6</sup>. A focused, high energy, beam of electrons is scanned over a thin specimen through atomic interaction back-scattered electrons, secondary electrons and X-rays are produced as seen in Figure 2.5 all providing specific imaging modes.

Transmitted electrons, collected on axis give bright field signals. These are electrons that have not been scattered by the sample or have been inelastically scattered, through angles of milliradians, under specific conditions the bright field mode of STEM is identical to that in TEM. STEM is able to provide benefits in dark field operation, with a unique imaging mode, High Angle Annular Dark Field (HAADF) imaging. Here the images are derived from elastically scattered electrons that have passed very close to the atomic nuclei of the sample. High resolution is achieved, meaning that it is possible to produce images that do not suffer from diffraction contrast, which can cause loss of structural information. The HAADF signal is proportional to  $Z^{3/2}$ , where  $Z$  is the atomic number.

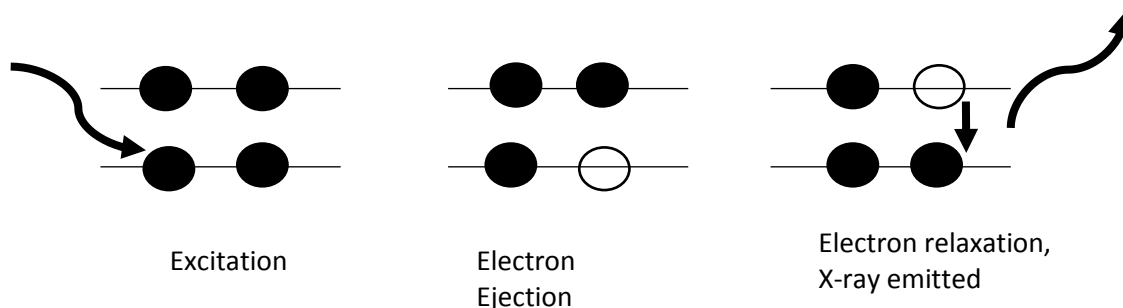
Secondary electron imaging is an additional benefit of STEM, where backscattered and secondary electrons are collected in a manner similar to that seen in SEM. As such it is possible to correlate surface information, from secondary electrons, with bulk information from the STEM mode. Secondary electrons are produced by the primary electron beam entering the sample or when backscattered electrons leave the sample<sup>5</sup>.



**Figure 2.5.** Schematic of detectable signals in electron microscopy, from a sample bombarded with a primary electron beam.

### 2.8.3. Energy Dispersive X-ray Spectroscopy (EDX).

EDX is a bulk characteristic technique that is used for elemental analysis. The interaction between an electron beam and an electron from within the atomic structure of the sample causes the emission of a core shell electron, producing a vacancy, this vacancy is filled by an outer shell electron and the excess energy is released in the form of an X-ray. The individual nature of the electronic structure of each element means that the energy of the emitted X-ray will be individual to each element and so it is possible to distinguish elements due to atomic number<sup>7</sup>.



**Figure 2.6.** Energy dispersive X-ray spectroscopy schematic.

### 2.9. X-ray photoelectron spectroscopy (XPS).

X-ray photoelectron spectroscopy is a surface sensitive characterisation technique that provides information about the oxidation state of species as well as chemical composition of the catalyst surface, to a depth of approximately 10 nm<sup>4</sup>. XPS is based on the photoelectric effect, where the adsorption of high energy X-rays by a core electron results in its emission. The kinetic energy of the ejected electron is dependent on energy of the incident X-rays, the work function of the spectrometer as well as the binding energy of the core electron.

The binding energy of each core electron is specific to each element, which also depends on the oxidation state of the element; as the oxidation state of the sample increases so does the binding energy associated with the core electrons. For a core electron to be emitted the energy of the incident X-ray must be greater than the binding energy. Indeed to be able to detect an electron the energy of the incident X-ray must be greater than that of the binding energy combined with the work function of the spectrometer. The excess energy is measured



as the kinetic energy of the electron. The work function of the spectrometer is the energy required to eject an electron from the Fermi level into the vacuum. The equation below summarises the photoelectric effect.

$$E_K = h\nu - E_B - \varphi$$

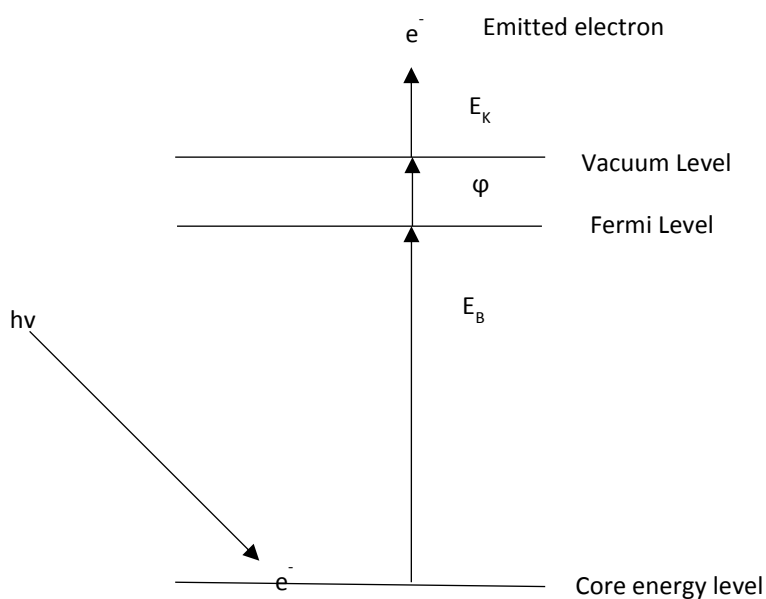
Where  $E_K$  = Kinetic energy of the ejected electron

$h\nu$  = photon energy

$E_B$  = binding energy

$\varphi$  = work function of spectrometer

Figure 2.7. represents a simplified energy level diagram of the photoelectric effect equation above. This shows that to eject an electron from a core energy level the energy of the incident X-ray is equal to the binding energy and kinetic energy of the electron, combined with the work function.



**Figure 2.7.** Energy level diagram to represent the energy barriers associated with the photoelectric effect.

As XPS is a sensitive technique it provides information about particle dispersion on a support. For a highly dispersed sample the intensity of the signal from the nanoparticles will be high, while in comparison the intensity of the signals associated with the support will be low.

Procedure : XPS analysis was carried out using a Kratos Axis Ultra-DLD spectrometer employing a monochromatic AlK $\alpha$  X-ray source (75-120 W) and analyzer pass energies of 160

eV ( for survey scans) or 40 eV (for detailed scans). Samples were mounted using double sided adhesive tape and analysed under ultra-high vacuum (UHV) ( $<5 \times 10^{-10}$  Torr). Binding energies were referenced to the C (1s) binding energy of adventitious carbon contamination which was taken to be 84.7 eV.

## 2.10. Temperature Programmed Desorption (TPD).

TPD is an extremely powerful tool for measuring the desorption of adsorbed molecules from a surface with increasing temperature. In TPD studies a sample equilibrated with an adsorbate is heated in a controlled manner. Desorption of the previously adsorbed species occurs when the thermal energy exceeds the adsorption energy. The temperature of desorption therefore indicates the strength of the bond between the adsorbent and the substrate. Quantification of the desorbed species occurs through the use of a TCD. The variation in the thermal conductivity of the gas mixture is measured, to produce a plot of thermal conductivity as a function of sample temperature, allowing for the quantification of adsorbed species. Materials with acidic sites are probed for their acidity using a basis species, such as  $\text{NH}_3$ , whilst basic materials are investigated using an acidic probe molecule, such as  $\text{CO}$ .

$\text{NH}_3$ -TPD was employed to probe the distribution of weak and strong acidic sites present (low and high temperature desorption respectively) and in turn allows for comparison of the acidity the materials investigated.

Procedure:

Temperature programmed desorption (TPD) was carried out using a Quantachrome Industries ChemBET TPR/TPD chemisorption analyser, fitted with a thermal conductivity detector (TCD). 50 mg of sample was pre-treated for 1 h at 130 °C ( $15^\circ\text{Cmin}^{-1}$ ) in He ( $80\text{ mlmin}^{-1}$ ). Ammonia was adsorbed at room temperature for 20 minutes to ensure saturation. Physisorbed ammonia was then removed at 100 °C (1h,  $15^\circ\text{Cmin}^{-1}$ ) in He ( $80\text{ mlmin}^{-1}$ ). Chemisorbed ammonia was subsequently desorbed by heating to 900 °C ( $15^\circ\text{Cmin}^{-1}$ ) in a flow of He ( $80\text{ ml min}^{-1}$ ) with the desorption monitored using a TCD with a current of 180 mV, and an attenuation of 1.

## 2.11. Infra-red Spectroscopy (IR).

Infra-red spectroscopy is an effective technique to clarify the structure of chemical compounds, it deals with the adsorption of light in the range of 0.8 – 1000  $\mu\text{m}$ . The spectral range is divided into three regions; near-IR (14000-400  $\text{cm}^{-1}$ ), mid-IR (4000-400 $\text{cm}^{-1}$ ) and far-IR (400-10 $\text{cm}^{-1}$ ). IR spectroscopy measures the adsorption of different IR frequencies when a sample is placed in the path of an IR beam. The adsorption of a given frequency of IR-radiation corresponds to the energies involved in bond vibrations (stretching and bending) in the molecule being studied. However not all vibrations can be observed, a general selection rule for the adsorption of an IR photon is that the dipole moment of the molecule must alter during the vibration. The group frequency concept allows functional groups in a molecule to be treated as independent oscillators. The strength of a bond in a functional group can be determined by the position of the bands in the resulting IR spectra, which is derived from Hooke's law, below.

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ where } \mu = \frac{m_A m_B}{m_A + m_B}$$

Where:  $\nu$  = the wavenumber of the vibration ( $\text{cm}^{-1}$ )

$c$  = the speed of light =  $2.998 \times 10^8 \text{ ms}^{-1}$

$k$  = force constant of the bond

$\mu$  = reduced mass (g) with  $m_i$  = the mass of vibrating atom  $i$  (g)

Therefore, functional groups with stronger bonds or consisting of lighter atoms or stronger bonds absorb IR radiation of higher wavelength than those consisting of weaker bonds or heavier atoms.

Several forms of IR spectroscopy can be utilised and within this work both transmission and diffuse reflection forms are employed. The primary difference between these two techniques being that; transmission spectroscopy applies IR radiation through the sample, while in diffuse reflection IR radiation is reflected off the sample surface. These two techniques can therefore be described as bulk and surface techniques respectively.

## 2.12. CO Chemisorption.

Chemisorption can be thought of as the titration of surface sites by an adsorbate, usually H<sub>2</sub>, O<sub>2</sub> or CO, which reacts only with the active phase to form a monolayer. Often it is used to determine metal dispersion, crystallite size and metal surface area on supported metal catalysts. From the experimentally measured adsorbed volume the number of adsorbed moles can be calculated as can the total number of surface atoms. It is then possible to calculate metal dispersion and surface area by knowing the loading of the metal on the support.

A relationship between the diameter of the metal cluster and its dispersion, which can be calculated through assumption that the cluster is spherical. The number of surface atoms can then be defined using the following equation.

$$N_s = \frac{\pi d^2}{S_M}$$

Where :  $N_s$  = number of surface atoms.

$\pi d^2$  = surface of the metal cluster.

$S_M$  = Atomic cross sectional area.

Procedure:

CO chemisorption analysis was achieved on a Quantachrome ChemBet equipped with a cold trap. Samples (0.05 g) were pre-treated at 100 °C (ramp 20 °C min<sup>-1</sup>) under helium for 1 hour prior to reduction in order to clean the surface. Analysis was performed by titrating 35 ul CO (BOC 99.99%, 25 ml min<sup>-1</sup>) over the sample until the stable TCD signal was achieved. CO was pulsed through the apparatus by-passing the sample 3 times for calibration.

## 2.13. References

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## Appendix. 2. 1

Analysis of reaction mixtures was conducted *via* gas chromatography. The following equations were used to determine cyclohexanone conversion (1, 2 and 3), selectivity towards cyclohexanone oxime (4) and yield of cyclohexanone oxime (5 and 6). Response factors were calculated for cyclohexanone (Figure A.1) and cyclohexanone oxime (Figure B.1) using diethylene glycol monoethyl ether as a standard.

$$(1) \text{ Cyclo. Conversion (\%)} = 100 - \text{Cyclo. Recovery (\%)}$$

$$(2) \text{ Cyclo. Recovery (\%)} = \left( \frac{\text{Final Mass of Cyclo. (g)}}{\text{Initial Mass of Cyclo.}} \right) \times 100$$

$$(3) \text{ Final Mass of Cyclo. (g)} = \left\{ \frac{\left( \frac{\text{GC counts of Cyclo.}}{\text{GC counts of STD-Y intercept from graph A}} \right)}{\left( \text{Slope from graph A} \times \text{Mass of STD (g)} \right)} \right\}$$

$$(4) \text{ Oxime Selectivity} = \frac{\text{Oxime Yield (\%)}}{\text{Cyclo. Conversion (\%)}} \times 100$$

$$(5) \text{ Oxime Yield (\%)} = \left\{ \frac{\left( \frac{\text{Mass of Oxime (g)}}{M_r \text{ Oxime}} \right)}{\left( \frac{\text{Initial Mass of Cyclo. (g)}}{M_r \text{ Cyclo.}} \right)} \right\} \times 100$$

$$(6) \text{ Mass of Oxime (g)} = \left\{ \frac{\left( \frac{\text{GC counts of Oxime}}{\text{GC counts of STD-Y intercept from graph B}} \right)}{\left( \text{Slope from graph B} \times \text{Mass of STD (g)} \right)} \right\}$$

Where:

Cyclo. = Cyclohexanone

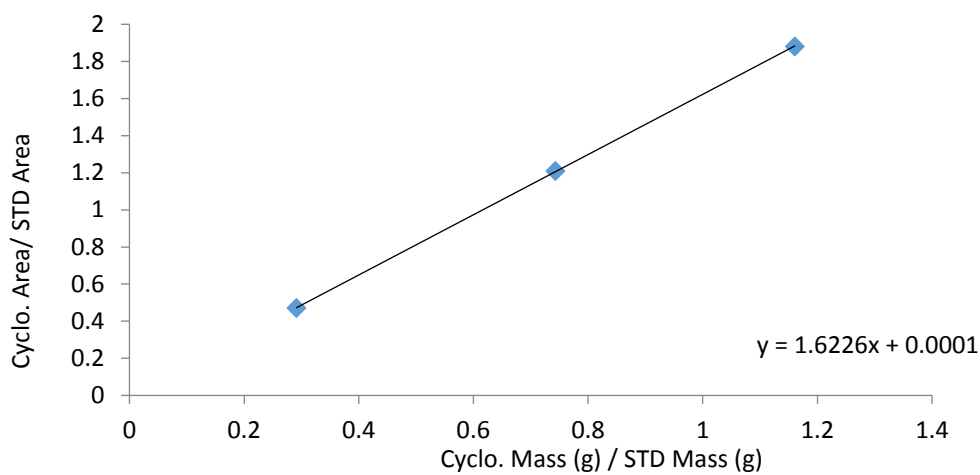
Oxime = Cyclohexanone Oxime

STD = Standard (diethylene glycol monoethyl ether)

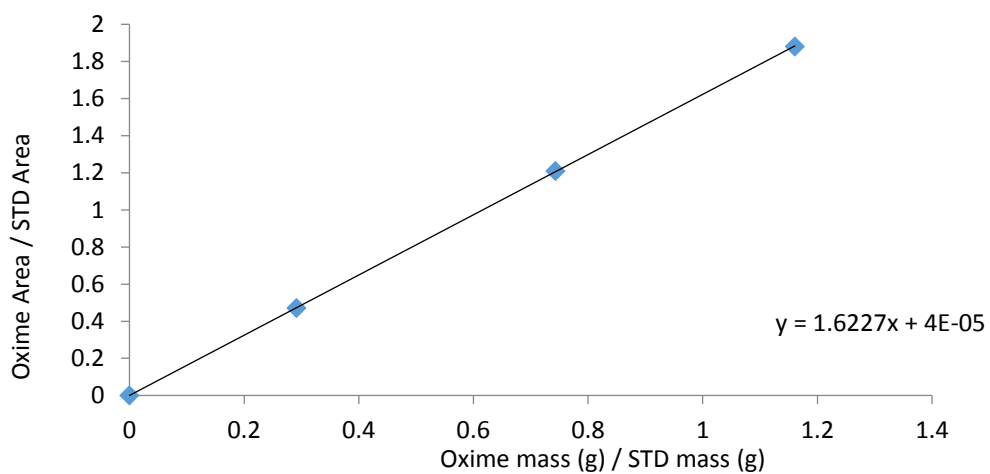
GC = Gas Chromatograph

$M_r$  = Molar mass

**Figure A.1** Obtained response factor for cyclohexanone with respect to diethylene glycol monoethyl ether standard



**Figure B.1** Obtained response factor for cyclohexanone oxime with respect to diethylene glycol monoethyl ether standard.



### 3. The Direct Synthesis of H<sub>2</sub>O<sub>2</sub> using supported Gold Palladium Catalysts and Heteropolyacid based additives.

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#### 3.1. Introduction.

Many studies have been carried out to produce heterogeneous catalysts with activity towards the direct synthesis of H<sub>2</sub>O<sub>2</sub>, from H<sub>2</sub> and O<sub>2</sub>, with the use of supported Pd catalysts prevalent in the literature and largely based upon the seminal work by Pospelova and co-workers<sup>1-3</sup>. However, these monometallic Pd catalysts, although highly active towards the direct synthesis of H<sub>2</sub>O<sub>2</sub> also have activity to its subsequent degradation<sup>4</sup>. The introduction of Au into a Pd-only catalyst has been shown to produce a significantly more active catalyst, with superior selectivity to the monometallic Pd analogue.<sup>5,6</sup> The utilisation of halides and acids, either as part of the reaction medium or incorporated into catalyst preparation are reported to limit the subsequent degradation pathways, in particular H<sub>2</sub>O<sub>2</sub> decomposition.<sup>7-9</sup> However the utilisation of halides and acidic reaction media can present some issues, in particular the cost of neutralising and replacing the promoters as well as corrosion caused to the reaction vessel and subsequent maintenance costs associated with such issues.

The almost super-acidic nature of heteropolyacids (HPAs) such as tungstophosphoric acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) has been well studied<sup>10</sup> and the ability to produce insoluble salts of these solid acids through the incorporation of cations such as Cs<sup>+</sup>, Rb<sup>+</sup> and K<sup>+</sup> has led to their investigation as acidic supports in the direct synthesis of H<sub>2</sub>O<sub>2</sub>. Indeed Park *et.al.* have studied Pd-exchanged heteropolyacids with varying Cs-content and shown that the most acidic catalyst (Pd<sub>0.15</sub>Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub>) was the most active towards the synthesis of H<sub>2</sub>O<sub>2</sub><sup>11</sup>. Sun *et.al.* have reported that Pd based catalysts utilising a heteropolyacid support show greater productivity and selectivity towards H<sub>2</sub>O<sub>2</sub> when compared to more conventional supports<sup>12</sup>. Hutchings and co-workers have investigated Au-Pd supported and exchanged heteropolyacids, under conditions deemed less conducive to H<sub>2</sub>O<sub>2</sub> synthesis and shown that these catalysts afford superior activity compared to catalysts previously investigated under optimised reaction conditions<sup>13 14</sup>. However both these studies do not investigate the extent of Cs incorporation into the H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> structure to a great extent, its effect on promoting catalytic activity towards the synthesis of H<sub>2</sub>O<sub>2</sub> or the combination of Cs<sub>x</sub>H<sub>3</sub>.



$x\text{PW}_{12}\text{O}_{40}$  salts and catalysts already established as active towards the direct synthesis of  $\text{H}_2\text{O}_2$ . Within this Chapter the extent of Cs incorporation in to  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  is explored in an attempt to improve catalytic activity towards  $\text{H}_2\text{O}_2$  synthesis.

In an attempt to improve catalytic activity towards the direct synthesis of  $\text{H}_2\text{O}_2$  the use of Cs-exchanged tungstophosphoric acid in addition to a well-established catalyst, known to be active towards  $\text{H}_2\text{O}_2$  synthesis. In this case 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  is studied. The degree of Cs exchange and the amount of Cs-exchanged tungstophosphoric acid promotor used, as an additive with 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  were investigated. The effect of these two parameters on catalytic activity towards the direct synthesis of  $\text{H}_2\text{O}_2$  and its subsequent degradation under standard reaction conditions, outlined in Chapter 2, were studied. Furthermore, reaction conditions were optimised, utilising the most effective Cs-exchanged additive and an investigation into the promotive role of Cs-exchanged tungstophosphoric acid on catalytic activity was carried out. Finally, reusability of these HPA-promoted catalyst systems was studied.

A supported Au-Pd catalyst was prepared using the standard wet impregnation technique using  $\text{PdCl}_2$  and  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  as metal precursors and  $\text{TiO}_2$  as the support, as outlined in Chapter 2, Section 2.2.1. While the metal exchanged heteropolyacids were produced via an ion exchange procedure, where the required metal nitrate and parent heteropolyacid were used as precursors.

All  $\text{H}_2\text{O}_2$  synthesis and degradation testing was carried out according to the procedures discussed previously in Chapter 2, unless otherwise stated. For reference a summary of the testing conditions are given below. Blank degradation reactions, in the absence of a catalyst were carried out on a regular basis to determine reactor contribution to  $\text{H}_2\text{O}_2$  degradation. If reactor contamination were determined to contribute to  $\text{H}_2\text{O}_2$  degradation these were removed using aqua-regia followed by thorough cleaning with water. A subsequent blank reaction was then carried out subsequent to catalysed reactions.

Rate of  $\text{H}_2\text{O}_2$  synthesis determined after reaction under standard reaction conditions:

5%  $\text{H}_2$  /  $\text{CO}_2$  (2.9 MPa) and 25%  $\text{O}_2$  /  $\text{CO}_2$  (1.1 MPa) , 8.5 g solvent (5.6 g methanol + 2.9 g  $\text{H}_2\text{O}$ ), 0.01 g catalyst, 2 °C , 1200 rpm, 30 mins.

Rate of H<sub>2</sub>O<sub>2</sub> degradation determined from the amount of H<sub>2</sub>O<sub>2</sub> that is hydrogenated under standard reaction conditions:

2.9 MPa 5% H<sub>2</sub> / CO<sub>2</sub>, 8.5 g solvent (5.6 g MeOH, 2.22 g H<sub>2</sub>O and 0.68 g H<sub>2</sub>O<sub>2</sub> (50 wt. %)), 0.01 g catalyst, 2 °C, 1200 rpm, 30 mins.

## 3.2. Results and discussion.

### 3.2.1. The direct synthesis of H<sub>2</sub>O<sub>2</sub> using 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> catalyst and Cs-exchanged heteropolyacids.

To determine whether heteropolyacid additives show intrinsic activity towards the direct synthesis of H<sub>2</sub>O<sub>2</sub>, a range of free and Cs – exchanged tungstophosphoric acids were assessed and the results are shown in Table 3.1

**Table 3.1.** Productivity and degradation of catalysts, towards H<sub>2</sub>O<sub>2</sub>, under standard reaction conditions.

Catalyst	Productivity / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	Degradation / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>
No catalyst	0	0
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	0	35
Cs <sub>0.1</sub> H <sub>2.9</sub> PW <sub>12</sub> O <sub>40</sub>	0	39
CsH <sub>2</sub> PW <sub>12</sub> O <sub>40</sub>	0	63
Cs <sub>2</sub> HPW <sub>12</sub> O <sub>40</sub>	0	88
Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub>	0	124
Cs <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	0	187
2.5 wt. % Au – 2.5 wt. % Pd/TiO <sub>2</sub>	64	213

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd /TiO<sub>2</sub> (0.01g) or Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> (0.01g), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g CH<sub>3</sub>OH + 2.9 g H<sub>2</sub>O (66 wt. % CH<sub>3</sub>OH), 2°C .

It can be observed in Table 3.1 that there is no H<sub>2</sub>O<sub>2</sub> formation or degradation in the absence of a AuPd catalyst or tungstophosphoric acid promotor. The productivity and degradation values observed for the 2.5 wt. % Au- 2.5 wt.% Pd / TiO<sub>2</sub> catalyst are 64 and 213 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> respectively. All Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> salts with and without Cs exchanged into the Keggin structure are observed to have no activity towards H<sub>2</sub>O<sub>2</sub> synthesis but are active towards its degradation. Indeed, the degradation activity for Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> is reported as 187 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> while the lower loaded Cs<sub>0.1</sub>H<sub>2.9</sub>PW<sub>12</sub>O<sub>40</sub> has much less degradation activity, 39 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>, comparable to the parent tungstophosphoric acid, with the activity of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> towards H<sub>2</sub>O<sub>2</sub> degradation observed to be 35 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>. A correlation between the extent of Cs loading and the degree of H<sub>2</sub>O<sub>2</sub> degradation can be made, with those additives with greater Cs-loading observed to be more active towards the degradation

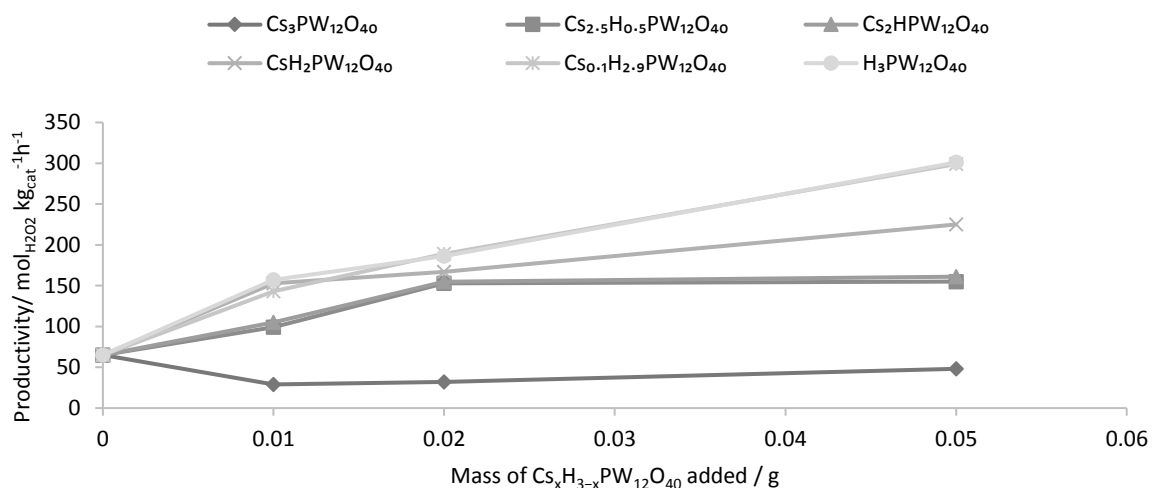
of  $\text{H}_2\text{O}_2$ . It is known that  $\text{H}_2\text{O}_2$  has greater stability under acidic reaction conditions and readily decomposes to  $\text{H}_2\text{O}$  in an alkaline medium. As such it is possible that by increasing the value of  $x$  in  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ , that is increasing Cs content, the surface acidity decreases and as such the extent of  $\text{H}_2\text{O}_2$  degradation increases.

It has been suggested by Park *et.al*<sup>15</sup>, who investigated the direct synthesis of  $\text{H}_2\text{O}_2$  using Pd exchanged tungstophosphoric acid, that by increasing Cs content it is possible to increase the surface acidity of the exchanged heteropolyacid, to a critical Cs loading; beyond this point surface acidity decreases. Dias and co-workers<sup>16</sup> report that surface acidity follows the following trend  $\text{H}_3\text{PW}_{12}\text{O}_{40} > \text{Cs}_2\text{HPW}_{12}\text{O}_{40} \approx \text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40} > \text{CsH}_2\text{PW}_{12}\text{O}_{40} \gg \text{Cs}_3\text{PW}_{12}\text{O}_{40}$ . This suggests that the role of surface acidity may not be the critical factor in determining the activity of Cs-exchanged HPAs towards  $\text{H}_2\text{O}_2$  degradation. However the general trend in the activity of the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts towards  $\text{H}_2\text{O}_2$  degradation is very similar to the trend in surface acidity reported by Dias and co-workers<sup>16</sup>.

It is suggested that the introduction of Cs reduces the solubility of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  through the formation of an insoluble Cs salt. Narasimharao *et.al*.<sup>17</sup> report the formation of insoluble Cs-exchanged  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  for  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  with values of  $x$  as little as 0.9. The ability of Cs-exchange into the Keggin unit to reduce the solubility of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  is discussed below.

### 3.2.2. The effect of Cs-exchanged of tungstophosphoric acid on the promotion of 2.5 wt. % Au – 2.5 wt. % Pd / $\text{TiO}_2$ towards the direct synthesis of $\text{H}_2\text{O}_2$ .

It is shown in Table 3.1 that decreasing the extent of Cs exchanged into the HPA structure results in a lower rate of  $\text{H}_2\text{O}_2$  degradation, when the additive is not used in conjunction with a catalyst that is active towards  $\text{H}_2\text{O}_2$  synthesis. The effect that the addition of Cs-exchanged HPAs (with varying Cs content) has on the direct synthesis of  $\text{H}_2\text{O}_2$  is shown in Figure 3.1



**Figure 3.1.**  $\text{H}_2\text{O}_2$  Productivity for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  and  $\text{Cs}_x\text{P}_{3-x}\text{W}_{12}\text{O}_{40}$  as a function of additive loading.

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  (0.01g),  $\text{Cs}_x\text{P}_{3-x}\text{W}_{12}\text{O}_{40}$  (X g), total pressure 580 psi,  $\text{H}_2$  /  $\text{O}_2$  = 0.525, 1200 rpm, 30 min, 5.6 g  $\text{CH}_3\text{OH}$  + 2.9 g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ), 2 °C.

It can be observed in Figure 3.1 that the addition of  $\text{Cs}_x\text{P}_{3-x}\text{W}_{12}\text{O}_{40}$ , with values of x ranging from 0 to 2.5, to 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  results in an increase in the rate of  $\text{H}_2\text{O}_2$  formation. While the addition of  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$  causes a decrease in productivity. Indeed with the addition of 0.01 g of  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$  productivity drops to a minimum value of 29  $\text{mol}_{\text{H}_2\text{O}_2}\text{Kg}_{\text{cata}}^{-1}\text{h}^{-1}$ , upon further addition of  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$  productivity slowly increases to reach a value of 48  $\text{mol}_{\text{H}_2\text{O}_2}\text{Kg}_{\text{cata}}^{-1}\text{h}^{-1}$  when 0.05g of  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$  is utilised. It is suggested that the increase in catalyst activity towards  $\text{H}_2\text{O}_2$  observed with increasing addition of  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$  is related to incomplete exchange of the protons within the Keggin structure. As such some promotional effect towards improving catalytic activity towards  $\text{H}_2\text{O}_2$  synthesis remains. It is suggested that the exact composition of the  $\text{Cs}_x\text{P}_{3-x}\text{W}_{12}\text{O}_{40}$  salts be investigated to determine the effectiveness of the ion exchange technique. However, it should be noted that regardless of the amount of  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$  added catalytic activity is still significantly lower than the activity observed when only the 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst is utilised (64  $\text{mol}_{\text{H}_2\text{O}_2}\text{Kg}_{\text{cat}}^{-1}\text{h}^{-1}$ ). For all  $\text{Cs}_x\text{P}_{3-x}\text{W}_{12}\text{O}_{40}$  additives investigated the rate of  $\text{H}_2\text{O}_2$  synthesis increases with increasing additive mass.

The rate of  $\text{H}_2\text{O}_2$  synthesis is observed to increase with the addition of  $\text{Cs}_x\text{P}_{3-x}\text{W}_{12}\text{O}_{40}$  according to the following order:  $\text{H}_3\text{PW}_{12}\text{O}_{40} = \text{Cs}_{0.1}\text{PW}_{12}\text{O}_{40} > \text{Cs}_1\text{PW}_{12}\text{O}_{40} > \text{Cs}_2\text{PW}_{12}\text{O}_{40} = \text{Cs}_{2.5}\text{PW}_{12}\text{O}_{40} > \text{Cs}_3\text{PW}_{12}\text{O}_{40}$ . It is observed that  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{Cs}_{0.1}\text{PW}_{12}\text{O}_{40}$  show approximately the same improvement towards  $\text{H}_2\text{O}_2$  synthesis, regardless of the amount utilised in addition to the catalyst, which is in good agreement with the data previously

reported in Table 3.1. It can also be observed that the rate of  $\text{H}_2\text{O}_2$  synthesis is comparable when  $\text{Cs}_2\text{PW}_{12}\text{O}_{40}$  and  $\text{Cs}_{2.5}\text{PW}_{12}\text{O}_{40}$  are employed as additives.

The effect that the addition of 0.05 g of Cs-exchanged and non Cs-exchanged  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  has on  $\text{H}_2$  conversion and selectivity, when these additives are used in conjunction with 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  is shown in Table 3.2

**Table 3.2.** The effect of Cs exchanged HPAs on  $\text{H}_2$  conversion and selectivity, under standard reaction conditions.

$\text{Cs}_x\text{P}_{3-x}\text{W}_{12}\text{O}_{40}$ added	Productivity / $\text{mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$	$\text{H}_2$ conversion / %	$\text{H}_2$ Selectivity / %
No $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$	64	21	61
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	301	70	85
$\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$	299	69	86
$\text{CsH}_2\text{PW}_{12}\text{O}_{40}$	225	66	63
$\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$	161	55	54
$\text{Cs}_3\text{PW}_{12}\text{O}_{40}$	48	47	22

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  (0.01g),  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  (0.05g), total pressure 580 psi,  $\text{H}_2$  /  $\text{O}_2$  = 0.525, 1200 rpm, 30 min, 5.6 g  $\text{CH}_3\text{OH}$  + 2.9 g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ),  $2^\circ\text{C}$ .

It is observed in Table 3.2 that the addition of  $\text{Cs}_x\text{P}_{3-x}\text{W}_{12}\text{O}_{40}$ , with or without the introduction of Cs into the Keggin structure, increases  $\text{H}_2$  conversion, when compared to 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst alone. The highest rate of  $\text{H}_2$  conversion is observed when  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  is utilised (70%) and this value is very similar to that observed for  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  (69%). Measurement of  $\text{H}_2$  selectivity shows that  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  with values of x varying from 0 to 3 can be divided into two groups; those where Cs loading is greater than or equal to  $\text{Cs}_{2.0}$  and those with Cs loading equal to or lower than  $\text{Cs}_{1.0}$ . The former group is observed to lead to a decrease in  $\text{H}_2$  selectivity, when compared to the 2.5 wt. % Au- 2.5 wt. % Pd/ $\text{TiO}_2$  catalyst with a significant decrease observed when  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$  is used alongside the catalyst, with  $\text{H}_2$  selectivity falling to 22%. The latter group is observed to lead to a significant increase in  $\text{H}_2$  selectivity with both  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  reported to improve selectivity to above 80%.

To understand these trends the ability of the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts to promote the leaching of Au and Pd from the  $\text{TiO}_2$  support as well as the solubility of the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salt were determined by analysis of the post reaction solution by MP-AES. In particular the concentration of Cs and W in the post reaction solution were quantified and results of these studies are shown in Table 3.3. Furthermore the effect that the addition of  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  of varying value of x has on the pH of the reaction solution prior to the reaction was measured and the results can be seen in Table 3.4.

**Table 3.3.** Leaching of Pd, Cs and W during the direct synthesis of H<sub>2</sub>O<sub>2</sub> using 2.5 wt. % Au – 2.5 wt.% Pd/TiO<sub>2</sub> and Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub>.

Catalyst	Pd / ppm	Au / ppm	Cs / ppm	W / ppm
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	9	0	0	1834
Cs <sub>0.1</sub> H <sub>2.9</sub> PW <sub>12</sub> O <sub>40</sub>	8	0	0.05	1723
CsH <sub>2</sub> PW <sub>12</sub> O <sub>40</sub>	5	0	0.6	1096
Cs <sub>2</sub> HPW <sub>12</sub> O <sub>40</sub>	2	0	183	564
Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub>	1	0	150	359
Cs <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	1	0	95	240

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> (0.01g), Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> (0.05g), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g CH<sub>3</sub>OH + 2.9 g H<sub>2</sub>O (66 wt. % CH<sub>3</sub>OH), 2°C.

Firstly it should be observed that no Au is detected in the post reaction solution, regardless of Cs content within the Cs<sub>x</sub>P<sub>3-x</sub>W<sub>12</sub>O<sub>40</sub> salt. In comparison Pd is detected in all post reaction solutions, regardless of Cs content. These observations may be explained by the greater support – metal interaction for Au in comparison to Pd or the greater propensity for Pd to be oxidised.

It is observed that as the value of x in Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> increases the amount of Pd detected in the post reaction solution decreases from 9 ppm when H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> is utilised to 1 ppm when Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> additive is used, as determined by analysis of the post reaction solution by MP-AES. It should be noted that the percentage of leached Pd when H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> is used as an additive is equivalent to 30 % of total Pd loading on the catalyst.

Investigation of the reaction solution by MP-AES shows that as the degree of Cs incorporation increases the solubility of Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> decreases. H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, Cs<sub>0.1</sub>PW<sub>12</sub>O<sub>40</sub> and Cs<sub>1</sub>PW<sub>12</sub>O<sub>40</sub> are all highly soluble in the reaction solution, with the concentration of W particularly high for these three Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> salts. The concentration of W is observed to decrease from 1843 ppm when H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> is utilised to 1096 ppm when CsH<sub>2</sub>PW<sub>12</sub>O<sub>40</sub> is utilised. Further addition of Cs decreases the concentration of W detected decreasing dramatically, reaching 240 ppm for the Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> additive. This suggests that incorporation of Cs is required to reduce the solubility of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>.

It is observed that the concentration of dissolved Cs within the reaction solution increases with the value of “x” in Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub>, passing through a maximum, of 183 ppm with Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub>. As Cs incorporation into the Keggin structure increases, as when Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> is used as an additive the concentration of Cs detected in the reaction solution decreases, to 95 ppm. This suggests that Cs incorporation is required to lower the solubility of the heteropolyacid. However, it is observed that even at the highest degree of Cs exchange, when the Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> additive is utilised, both Cs (95 ppm) and W (240 ppm) are detected in the reaction solution suggesting that these materials are still partially soluble.

The effect of the Cs content within the Keggin unit on pH of the reaction solution prior to the reaction was measured and the results are outlined in Table 3.4.

**Table 3.4.** The pH of the reaction solution for the direct synthesis of  $\text{H}_2\text{O}_2$  using 2.5 wt. % Au – 2.5 wt.% Pd/ $\text{TiO}_2$  and  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$

Catalyst	pH	Productivity/ $\text{mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$
No catalyst	7	0
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	2.66	301
$\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$	2.68	299
$\text{CsH}_2\text{PW}_{12}\text{O}_{40}$	3.33	225
$\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$	3.82	161
$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$	3.90	155
$\text{Cs}_3\text{PW}_{12}\text{O}_{40}$	6.30	48
Au Pd/ $\text{TiO}_2$	7	64

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd / $\text{TiO}_2$  (0.01g),  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  (0.05g), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 5.6 g  $\text{CH}_3\text{OH}$  + 2.9 g  $\text{H}_2\text{O}$  (66w. %  $\text{CH}_3\text{OH}$ ),  $2^\circ\text{C}$ .

It is observed that the pH of the reaction solution decreases with the addition of all HPA additives. This is the most pronounced for the free Cs-acid  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  (pH 2.66 and 2.68 respectively). Catalytic activity towards the direct synthesis of  $\text{H}_2\text{O}_2$  is observed to correlate with the pH of the reaction solution, with the exception of  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$ . Interestingly the addition of  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$  lowers the pH of the reaction solution but does not improve catalytic activity towards  $\text{H}_2\text{O}_2$  formation. As Cs incorporation into the HPA structure decreases the pH of the reaction solution decreases. Through addition of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  the reaction solution pH is lowered to 2.68, this is very similar to that observed when the  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  additive is utilised (2.66) in addition to the 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst. It is known that acidic reaction conditions are beneficial to  $\text{H}_2\text{O}_2$  stability<sup>18</sup> and it is suggested that the incorporation of Cs exchanged HPAs and the resulting decrease in pH play a significant role in improving catalytic activity towards the formation of  $\text{H}_2\text{O}_2$ .

Table 3.5 shows the activity of the reaction solution towards  $\text{H}_2\text{O}_2$  synthesis. After a standard reaction with 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  (0.01g) and  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  (0.05g) the catalyst is removed by filtration. The reaction solution was then investigated for activity towards  $\text{H}_2\text{O}_2$  synthesis.

**Table 3.5.** H<sub>2</sub>O<sub>2</sub> Productivity for the reaction solution of 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> and Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>.

Catalyst	Leached Pd / ppm	Leached Au / ppm	Net Productivity / mol <sub>H2O2</sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	H <sub>2</sub> conversion / %	H <sub>2</sub> Selectivity / %
No Cs <sub>x</sub> P <sub>3-x</sub> W <sub>12</sub> O <sub>40</sub>	<b>n.d</b>	0	0	0	0
H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	9	0	19	7	75
Cs <sub>0.1</sub> H <sub>2.9</sub> PW <sub>12</sub> O <sub>40</sub>	8	0	17	7	74
CsH <sub>2</sub> PW <sub>12</sub> O <sub>40</sub>	5	0	12	5	72
Cs <sub>2</sub> HPW <sub>12</sub> O <sub>40</sub>	1	0	3	2	73
Cs <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	1	0	3	2	71

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> (0.01g), Cs<sub>x</sub>P<sub>3-x</sub>W<sub>12</sub>O<sub>40</sub> (0.05 g), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g CH<sub>3</sub>OH + 2.9 g H<sub>2</sub>O (66 wt. % CH<sub>3</sub>OH), 2 °C.

Where **n.d.** = none detected.

It is observed that when the 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> catalyst is used in the absence of a HPA promotor there is no leached metal detected and the reaction solution has no activity towards the formation of H<sub>2</sub>O<sub>2</sub>. Furthermore, it can be observed that only Pd is leached from the catalyst when it is used in addition to the Cs<sub>x</sub>P<sub>3-x</sub>W<sub>12</sub>O<sub>40</sub> salt, regardless of the extent of Cs incorporation. It should be noted that no Au is detected within the reaction solution, possibly suggesting that the metal – support interaction for Au is greater than for Pd.

It is possible to report that there is some homogenous activity towards the direct synthesis of H<sub>2</sub>O<sub>2</sub> for reaction solutions where heteropolyacid promoters were used in addition to 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub>. Indeed a general trend can be discerned whereby net activity towards H<sub>2</sub>O<sub>2</sub> formation decreases as the value of “x” in Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> increases, from 19 to 3 mol<sub>H2O2</sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> as Cs incorporation increases from H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> to Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>. This activity can be related to Pd content within the reaction solution, regardless of Cs content, Pd is leached from the catalyst support. The extent of leaching decreases as the Cs content increases, with a maximum of 9 ppm Pd detected when the H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> additive is utilised. This correlates with the activity towards H<sub>2</sub>O<sub>2</sub> synthesis. However, as stated previously 9 ppm Pd can be equated to approximately 30 % of the total Pd present on the catalyst. It may be expected that the activity of the leached metal in the reaction solution may be greater than that observed, it is suggested that the leached Pd is deposited on the liner of the reactor limiting activity towards the direct synthesis of H<sub>2</sub>O<sub>2</sub>. However further investigation into this is still required.

As expected given the relatively low values of productivities observed, the extent of H<sub>2</sub> conversion is particularly low, with the greatest H<sub>2</sub> conversion observed for the reaction solutions when both H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and Cs<sub>0.1</sub>H<sub>2.9</sub>PW<sub>12</sub>O<sub>40</sub> are utilised, with H<sub>2</sub> conversion of 7 %

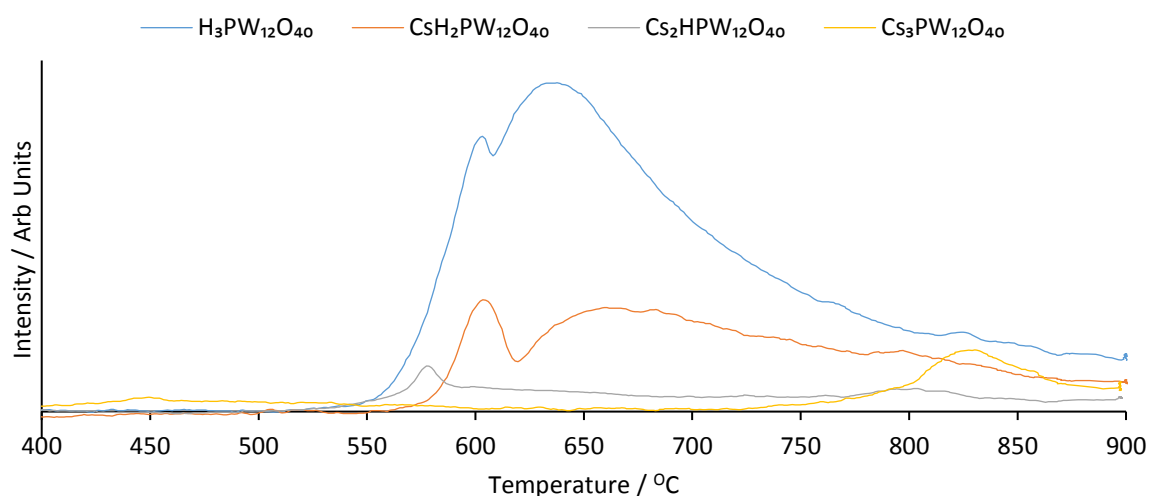


reported when both of these additives are used. In comparison, when these two additives are used in addition to 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> in a standard reaction H<sub>2</sub> conversion is much greater, with values of 70 and 69 % reported for H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and Cs<sub>0.1</sub>H<sub>2.9</sub>PW<sub>12</sub>O<sub>40</sub> respectively .

Unlike for H<sub>2</sub> conversion H<sub>2</sub> selectivity is high, with values of over 70 % reported regardless of Cs content and this is expected as H<sub>2</sub> conversion is particularly low. Lunsford and co-workers<sup>19</sup> have previously established the role of leached Pd for the direct synthesis, when 5 wt. % Pd / SiO<sub>2</sub> is utilised in addition to 1.0 M HCl and they attribute the loss of Pd to the presence of HCl in the reaction solution and the formation of PdCl<sub>4</sub><sup>2-</sup>. Indeed upon removal of the heterogeneous catalyst they report a net increase in H<sub>2</sub>O<sub>2</sub> concentration of approximately 0.02 wt. % H<sub>2</sub>O<sub>2</sub>. This is similar to the net increase in wt. % H<sub>2</sub>O<sub>2</sub> observed upon removal of the 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> catalyst when used in addition to H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>.

These results demonstrate that the presence of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>, is able to promote the leaching of Pd from the catalyst support and that as Cs exchange into the Keggin structure increases the extent of Pd leaching decreases. Furthermore it has been shown that the leached Pd has some activity towards the direct synthesis of H<sub>2</sub>O<sub>2</sub> and although this activity is limited when the reaction solution is investigated for activity towards the direct synthesis of H<sub>2</sub>O<sub>2</sub> the contribution of the leached Pd may be greater during a standard reaction. That is when the 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> catalyst is used in addition with Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub>.

Further analysis of the Cs-exchanged HPAs was carried out using NH<sub>3</sub>-TPD and the results are seen in Figure 3.2.

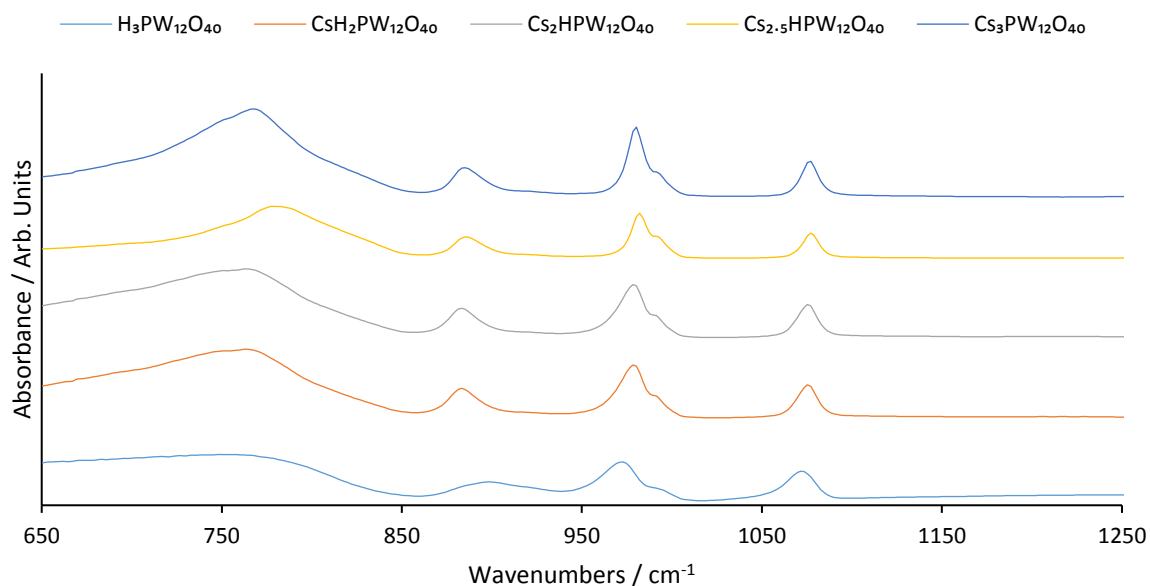


**Figure 3.2.** NH<sub>3</sub>-TPD of in Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> salts where x = 0, 1, 2 and 3.

It can be observed in Figure 3.2 that there is a correlation between acidity and Cs content. A trend is observed where acidity increases in the following order:  $\text{H}_3\text{PW}_{12}\text{O}_{40} > \text{Cs}_1\text{PW}_{12}\text{O}_{40} > \text{Cs}_2\text{PW}_{12}\text{O}_{40} > \text{Cs}_3\text{PW}_{12}\text{O}_{40}$ . These results are in good agreement with previous studies, which show a decrease of the acidity with an increase of the Cs content<sup>20</sup>.

The Keggin structure of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  has previously been reported to consist of a  $\text{PO}_4$  tetrahedron surrounded by twelve  $\text{WO}_6$  octahedra, which share edges in  $\text{W}_3\text{O}_{13}$  triad groups and corners between each triad through oxygen atoms<sup>21</sup>. From the structure it is possible to deduce four types of oxygen atoms, which are reported to provide for characteristic infrared bands in the range  $1200 - 700 \text{ cm}^{-1}$ . The exact position of these bands are known to depend upon the extent of hydration of the heteropolyacid<sup>22</sup> and the nature of the counter cation present<sup>23</sup>.

FTIR spectra of the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts were collected after preparation and calcination ( $300^\circ\text{C}$ , 2h, static air). The spectra of the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts are shown in Figure 3.3.

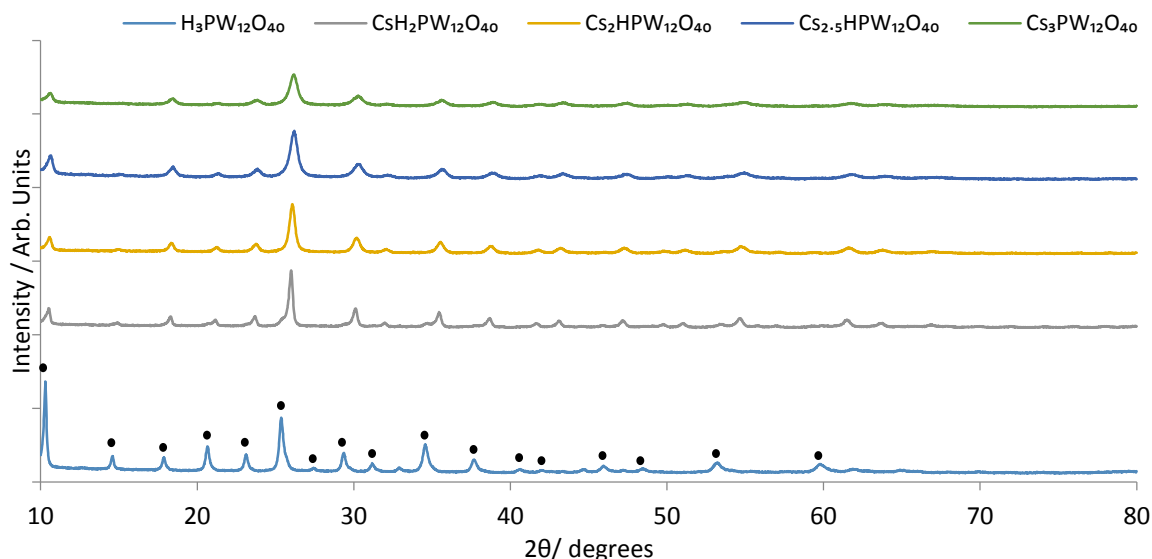


**Figure 3.3.** FTIR spectra of  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts after calcination at  $200^\circ\text{C}$ , 3h, static air.

The Keggin structure of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  has previously been reported to consist of a  $\text{PO}_4$  tetrahedron surrounded by twelve  $\text{WO}_6$  octahedra, which share edges in  $\text{W}_3\text{O}_{13}$  triad groups and corners between each triad through oxygen atoms. From the structure it is possible to deduce four types of oxygen atoms, which are reported to provide four characteristic bands in the range  $1200 - 700 \text{ cm}^{-1}$ . The exact position of these bands are known to depend upon the extent of hydration of the heteropolyacid and the nature of the counter cation present<sup>21</sup>.

It is possible to observe four distinct infrared bands in Figure 3.3 and it possible to assign these as follows;  $\nu(\text{P-O}) = 1080 \text{ cm}^{-1}$ ,  $\nu(\text{W-O}_c\text{-W}) = 883 \text{ cm}^{-1}$ ,  $\nu(\text{W-O}_e\text{-W}) = 784 \text{ cm}^{-1}$ . However the typical vibration of  $\nu(\text{W=O}) = 983 \text{ cm}^{-1}$  of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (HPA) can be observed to split into two components at 983 and 995  $\text{cm}^{-1}$ . This splitting can be assigned to W=O associated with  $\text{H}^+(\text{H}_2\text{O})_n$  species (983  $\text{cm}^{-1}$ ), as in hydrated  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and W=O interacting with  $\text{Cs}^+$  ions (995  $\text{cm}^{-1}$ ), this is in keeping with previous investigations reported by Essayem *et.al.*<sup>22</sup> the weaker interactions of  $\text{Cs}^+$  with W=O causes a strengthening of the latter bonds owing to its increase in double bond character, resulting in a higher frequency shift.

XRD patterns were also recorded for all the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts and are reported in Figure 3.4.



**Figure 3.4.** X-ray diffractogram of  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts, where  $x = 0-3$ , calcined 200 °C in static air, ramp rate = 20 °C min<sup>-1</sup>. ●:  $\text{H}_3\text{PW}_{12}\text{O}_{40}$

Figure 3.4 shows a sharp, intense diffraction pattern for the parent heteropolyacid indicating that the tungstophosphoric acid parent material is highly crystalline. Upon incorporation of  $\text{Cs}^+$  the reflections broaden and decrease in intensity indicating a loss in crystallinity. The detected reflections of the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts are consistent with the cubic structure of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (ICDD number 00-050-0657) as the catalysts prepared have similar  $\text{Cs}^+$  content. The main reflections associated with the  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  parent material are shifted towards higher  $2\theta$  values in the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts, consistent with an expansion of the tungstophosphoric acid unit cell upon introduction of Cs.

Surface area was measured using nitrogen adsorption for all the samples and is shown in Table 3.6.

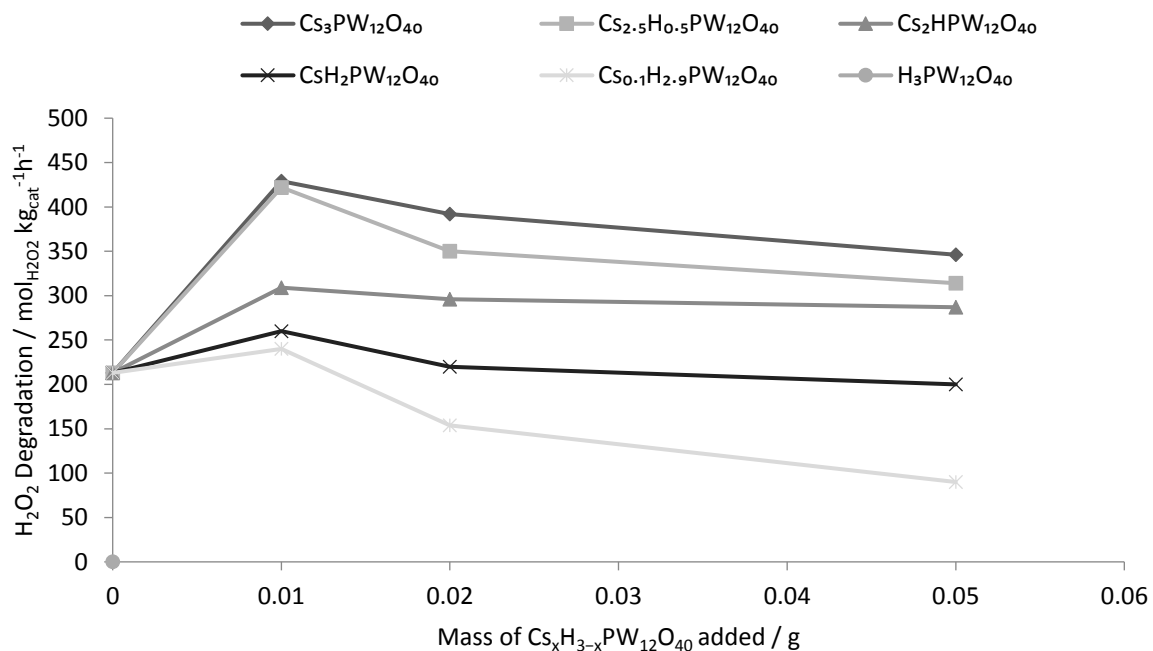
**Table 3.6.** BET surface area of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  with varied levels of  $\text{Cs}^+$  incorporation.

Catalyst	Surface area / $\text{m}^2\text{g}^{-1}$
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	0.52
$\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$	0.47
$\text{CsH}_2\text{PW}_{12}\text{O}_{40}$	3.50
$\text{Cs}_{1.5}\text{H}_{1.5}\text{PW}_{12}\text{O}_{40}$	6.82
$\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$	49.67
$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$	111.50
$\text{Cs}_3\text{PW}_{12}\text{O}_{40}$	121.13

Catalysts calcined 2 h, 300 °C, static air, ramp = 20 °C min<sup>-1</sup>

A trend was observed where those samples with greater  $\text{Cs}^+$  loading demonstrated greater surface areas. The  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$  solid acid additive showed the highest surface area of 121  $\text{m}^2\text{g}^{-1}$ . This correlates well with XRD analysis of these materials, which shows that with increasing degree of  $\text{Cs}^+$  incorporation there is a decrease in crystallinity of the material. Interestingly the additives that provide the greatest promotion towards  $\text{H}_2\text{O}_2$  synthesis have the lowest surface area, with the addition of  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$  lowering catalytic activity towards  $\text{H}_2\text{O}_2$  synthesis, from 64 to 48  $\text{mol}_{\text{H}_2\text{O}_2}\text{Kg}_{\text{cat}}^{-1}\text{h}^{-1}$ . The addition of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ , with a surface area of 0.52  $\text{m}^2\text{g}^{-1}$  improves catalytic activity by a factor of approximately 3.7 to 239  $\text{mol}_{\text{H}_2\text{O}_2}\text{Kg}_{\text{cat}}^{-1}\text{h}^{-1}$  suggesting that this characteristic is not important in improving catalytic activity towards  $\text{H}_2\text{O}_2$  synthesis. This enhancement can be related to both the amount of Cs leached from the Keggin structure and the pH of the reaction solution when the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts are used in addition to the 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst with the salts containing less Cs offering greater acidity and therefore improved  $\text{H}_2\text{O}_2$  stability in addition to a and a lower amount of Cs being introduced into reaction solution. As such the extent of  $\text{H}_2\text{O}_2$  degradation is decreased in comparison to when the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts with greater Cs incorporation are utilised in addition to the catalyst.

It was observed in Figure 3.1 that the utilisation of  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts in addition to 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  can dramatically enhance or hinder the formation of  $\text{H}_2\text{O}_2$ . With catalytic activity seen to increase as Cs content decreases. Further investigation into the ability of  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts to promote catalytic activity towards the degradation of  $\text{H}_2\text{O}_2$  can be seen in Figure 3.5.



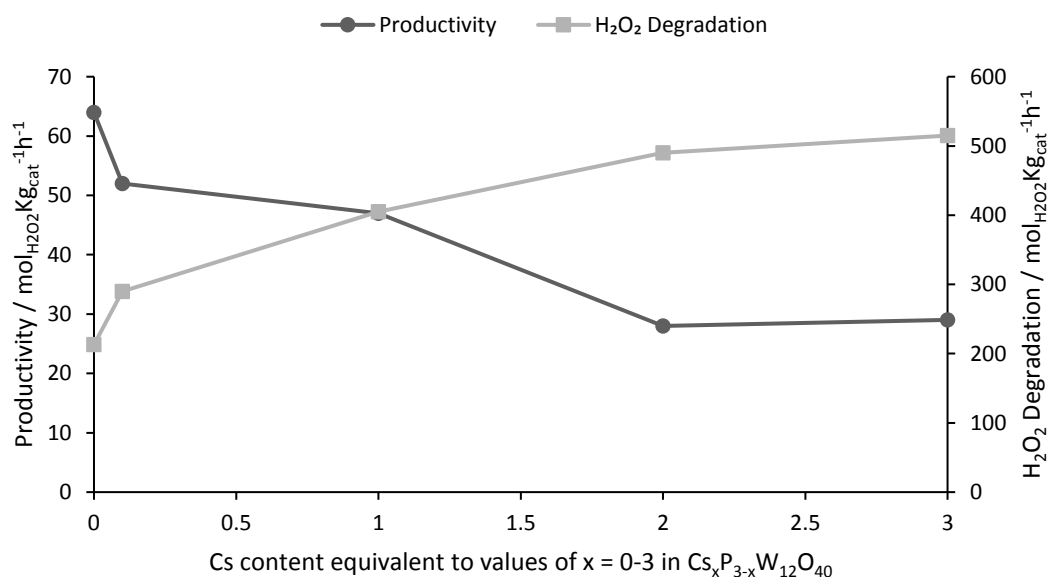
**Figure 3.5.**  $\text{H}_2\text{O}_2$  Degradation for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  and  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$  as a function of additive loading.

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  (0.01g),  $\text{Cs}_x\text{P}_{3-x}\text{W}_{12}\text{O}_{40}$  (X g), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 5.6 g  $\text{CH}_3\text{OH}$  + 2.9 g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ), 2 °C.

It can be observed, in Figure 3.5, that the addition of 0.01g Cs-exchanged or non-exchanged tungstophosphoric acid results in an increase in the overall degradation of  $\text{H}_2\text{O}_2$ , from 213  $\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1}\text{h}^{-1}$  for the 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst only. This is expected as it has been shown (Table 3.1) that these materials have some activity towards the degradation of  $\text{H}_2\text{O}_2$ . The increase in  $\text{H}_2\text{O}_2$  degradation is observed to correlate with Cs loading, again as reported previously in Table 3.1, with the greatest increase reported when  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$  is utilised in addition to the 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst. The rate of  $\text{H}_2\text{O}_2$  degradation increases from 213 to 429  $\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1}\text{h}^{-1}$  when 0.01g of  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$  is combined with 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$ . This increase in  $\text{H}_2\text{O}_2$  degradation with HPA addition is observed regardless of Cs loading, when 0.01 g of the additive is utilised.

Further addition of HPA decreases the rate of  $\text{H}_2\text{O}_2$  degradation. This decrease in  $\text{H}_2\text{O}_2$  degradation correlates with Cs content; that is the lower the Cs content the greater the decrease in  $\text{H}_2\text{O}_2$  degradation. It can be observed that with the addition of 0.05g of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  the rate of  $\text{H}_2\text{O}_2$  degradation decreases to 90  $\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1}\text{h}^{-1}$ , this is very similar to that observed when the non Cs substituted  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  is used in addition to the 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst (83  $\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1}\text{h}^{-1}$ ).

To understand the effect of Cs in the synthesis and degradation of  $\text{H}_2\text{O}_2$  Cs has been added to 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  in the form of  $\text{CsNO}_3$ . The concentration of Cs used is equivalent to that present when 0.05g of the Cs substituted  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  is utilised as an additive for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  and the results are shown in Figure 3.6.



**Figure 3.6.**  $\text{H}_2\text{O}_2$  Synthesis and Degradation for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  and  $\text{CsNO}_3$  as a function of  $\text{CsNO}_3$  loading.

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  (0.01g),  $\text{CsNO}_3$  (X g), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 5.6 g  $\text{CH}_3\text{OH}$  + 2.9 g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ), 2  $^\circ\text{C}$ .

It is observed that as the Cs concentration increases the rate of  $\text{H}_2\text{O}_2$  synthesis decreases, from  $64 \text{ mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$  to a minimum of  $29 \text{ mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$  when a concentration of Cs equivalent to that present in  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$  is utilised. This correlates with an increase in the degradation of  $\text{H}_2\text{O}_2$ , which increases to a maximum of  $515 \text{ mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$  when Cs concentration is at a maximum. Further investigation was then conducted to determine the activity of Cs towards both the direct synthesis and degradation of  $\text{H}_2\text{O}_2$  in the absence of the 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst. The results are shown in Table 3.7.

**Table 3.7.** The activity of  $\text{CsNO}_3$  towards the direct synthesis and degradation of  $\text{H}_2\text{O}_2$ .

[Cs] equivalent to that in $\text{Cs}_x\text{P}_{3-x}\text{W}_{12}\text{O}_{40}$	Productivity / $\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$	$\text{H}_2\text{O}_2$ Degradation / $\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$
No catalyst	0	0
$\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$	0	26
$\text{CsH}_2\text{PW}_{12}\text{O}_{40}$	0	125
$\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$	0	178
$\text{Cs}_3\text{PW}_{12}\text{O}_{40}$	0	215

**Reaction conditions for  $\text{H}_2\text{O}_2$  degradation:**  $\text{CsNO}_3$  (X g), total pressure 420 psi, 5 %  $\text{H}_2$  /  $\text{CO}_2$ , 1200 rpm, 30 min, 5.6 g  $\text{CH}_3\text{OH}$  + 2.22 g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ), 0.68g  $\text{H}_2\text{O}_2$  (50 wt. %) 2  $^\circ\text{C}$ .

It can be observed that Cs plays a significant role in the degradation of H<sub>2</sub>O<sub>2</sub>. Indeed, as the concentration of Cs in the reaction solution increases so does the activity towards the degradation of H<sub>2</sub>O<sub>2</sub>. It was shown in Table 3.1 that increasing the Cs content within the HPA structure results in an increase in the degradation of H<sub>2</sub>O<sub>2</sub> and a general trend can be observed in Table 3.3; that as Cs content within the Keggin structure increases so does the amount of leached Cs. It is possible to conclude that the increase in H<sub>2</sub>O<sub>2</sub> degradation observed with the addition of Cs<sub>x</sub>P<sub>3-x</sub>W<sub>12</sub>O<sub>40</sub> salts may be related to the extent of Cs exchange.

The utilisation of tungstophosphoric acid with lower Cs incorporation as an additive to 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> leads to a greater improvement in catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis, than the utilisation of the Cs incorporated salts with greater Cs content. It has been demonstrated that as the amount of Cs introduced into the Keggin cage structure decreases there is an increase in surface acidity and a decrease in the pH of the methanol-water working solution. However reaction solution pH remains lower than that observed when no additive is present. The effect of Cs-heteropolyacids have on solvent pH is investigated in Section 3.2.5.2

### 3.2.3. The effect of adding Cs<sub>0.1</sub>H<sub>2.9</sub>PW<sub>12</sub>O<sub>40</sub> to supported bimetallic catalysts.

The effectiveness of adding Cs<sub>0.1</sub>H<sub>2.9</sub>PW<sub>12</sub>O<sub>40</sub> to 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> led to the investigation of adding this acid additive to other catalysts known for their activity towards H<sub>2</sub>O<sub>2</sub> direct synthesis, namely 2.5 wt. % Sn – 2.5 wt. % Pd / TiO<sub>2</sub>, 2.5 wt. % Au – 2.5 wt. % Pd / Acid washed Carbon and 2.5 wt. % Au – 2.5 wt. % Pd / ZrO<sub>2</sub>. The results of this investigation are seen in Table 3.8.

**Table 3.8.** The effect of adding Cs<sub>0.1</sub>H<sub>2.9</sub>PW<sub>12</sub>O<sub>40</sub> to supported bimetallic catalysts, 2.5 wt. % Sn – 2.5 wt. % Pd / TiO<sub>2</sub>, 2.5 wt. % Au – 2.5 wt. % Pd / Acid washed Carbon and 2.5 Wt. % Au – 2.5 wt. % Pd / ZrO<sub>2</sub>.

Catalyst	Productivity / mol <sub>H2O2</sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	wt. % H <sub>2</sub> O <sub>2</sub>
2.5 wt. % Au – 2.5 wt. % Pd / TiO <sub>2</sub>	64	0.13
2.5 wt. % Au – 2.5 wt. % Pd / TiO <sub>2</sub> + Cs <sub>0.1</sub> H <sub>2.9</sub> PW <sub>12</sub> O <sub>40</sub>	299	0.60
2.5 wt. % Sn – 2.5 wt. % Pd / TiO <sub>2</sub>	60	0.10
2.5 wt. % Sn – 2.5 wt. % Pd / TiO <sub>2</sub> + Cs <sub>0.1</sub> H <sub>2.9</sub> PW <sub>12</sub> O <sub>40</sub>	134	0.27
2.5 wt. % Au – 2.5 wt. % Pd / Acid washed Carbon	190	0.38
2.5 wt. % Au – 2.5 wt. % Pd / Acid washed Carbon + Cs <sub>0.1</sub> H <sub>2.9</sub> PW <sub>12</sub> O <sub>40</sub>	348	0.70
2.5 wt. % Au – 2.5 wt. % Pd / ZrO <sub>2</sub>	76	0.15
2.5 wt. % Au – 2.5 wt. % Pd / ZrO <sub>2</sub> + Cs <sub>0.1</sub> H <sub>2.9</sub> PW <sub>12</sub> O <sub>40</sub>	210	0.43

**Reaction conditions:** Catalyst (0.01 g), Cs<sub>0.1</sub>H<sub>2.9</sub>PW<sub>12</sub>O<sub>40</sub> (0.05 g), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g CH<sub>3</sub>OH + 2.9 g H<sub>2</sub>O (66 wt. % CH<sub>3</sub>OH), 2 °C.  
Catalysts calcined 3 h, 400 °C, static air, ramp rate = 20 °C min<sup>-1</sup>

As can be observed in Table 3.8 when adding 0.05g of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  to these catalysts a dramatic increase is observed in both productivity and Wt. %  $\text{H}_2\text{O}_2$ , under standard reaction conditions. It can therefore be determined that the promotive effect first observed for the  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  - 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  system is also present in other  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  – catalyst systems, although the nature of this promotion requires further investigation before it is fully understood. The use of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  in addition to 2.5 wt. % Au – 2.5 wt. % Pd / Acid washed Carbon is observed to lead to a significant yield of  $\text{H}_2\text{O}_2$ , with a concentration of 0.7 wt.%. Further investigation and optimisation of reaction conditions of this system may lead to a significant enhancement in yield of  $\text{H}_2\text{O}_2$ .

It is suggested that some contribution to the increased catalytic activity towards  $\text{H}_2\text{O}_2$  synthesis may be attributed to the leaching of active metals from the support and it is suggested that further work be conducted to determine the extent of leaching when  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  is used in addition to the catalysts shown in Table 3.8. It has previously been shown (Table 3.3) that when using a  $\text{TiO}_2$  support significant leaching of Pd can occur. It may be that with varying the support the extent of metal leaching changes and through catalyst design it may be possible to inhibit the leaching of metals from the support. For example it may be possible to limit the extent of leaching by exposing the catalyst to increased catalyst calcination temperature, although this is likely to decrease catalytic activity. It may be possible to reach a compromise between catalyst activity and stability.

#### 3.2.4. The Effect of Reaction Conditions on the direct synthesis of $\text{H}_2\text{O}_2$ using $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$ as a solid acid additive for 2.5 wt. % Au – 2.5 wt. % Pd / $\text{TiO}_2$ .

Amongst other catalysts 2.5 wt. % Au - 2.5 wt. % Pd /  $\text{TiO}_2$  has been established as a catalyst that is active towards the direct synthesis of hydrogen peroxide. It was decided to optimise the reaction conditions used when  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  is added as an acid additive for this catalyst, in an attempt to increase overall yield of  $\text{H}_2\text{O}_2$ . This additive has been observed to provide the greatest improvement in catalytic activity, when compared to higher loadings of Cs exchange.

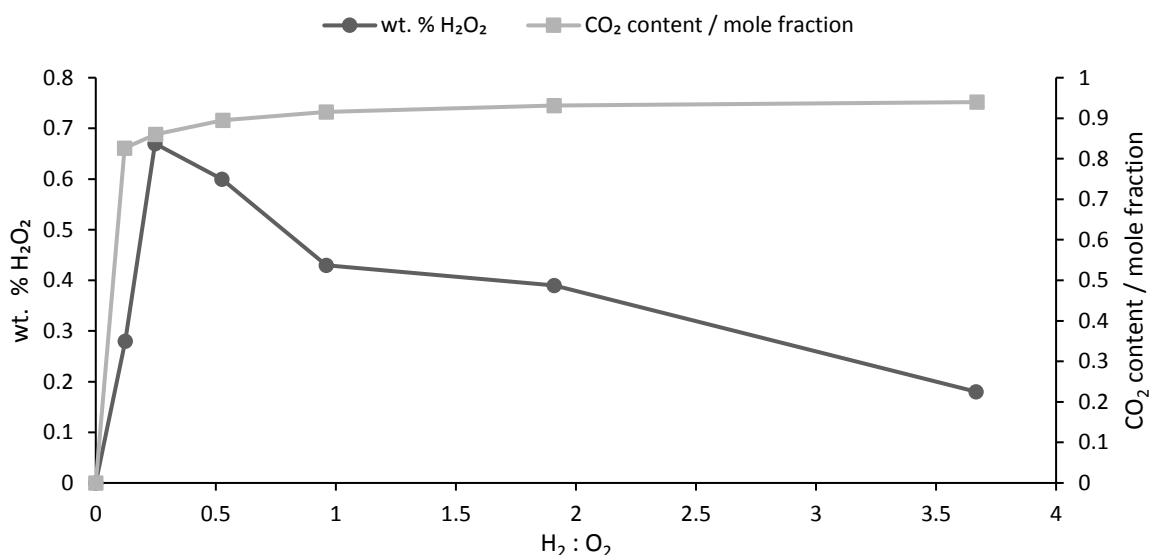
Several reaction conditions are investigated including; reaction temperature, solvent composition and reaction time and the results will be presented in the following Sections.



It should be noted that a number of parameters can influence catalyst productivity and degradation and prevent a true representation of catalyst activity and selectivity being determined, including reaction time and catalyst mass. This is because both parameters are expressed in terms of moles of  $\text{H}_2\text{O}_2$  produced / degraded per Kg of catalyst per hour. As such the overall yield of  $\text{H}_2\text{O}_2$  (wt. %) and degradation of  $\text{H}_2\text{O}_2$  (% degradation) are used throughout this section to allow for better normalisation of catalyst activity.

#### 3.2.4.1. Effect of gas feed composition.

Figure 3.7 shows the effect of reactant gas ratio on the direct synthesis of  $\text{H}_2\text{O}_2$ . As  $\text{H}_2\text{O}_2$  degradation is determined in the presence of  $\text{H}_2$  /  $\text{CO}_2$  only, it is not possible to determine the effect of  $\text{H}_2$  :  $\text{O}_2$  ratio on this parameter.



**Figure 3.7**  $\text{H}_2\text{O}_2$  wt. % for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  and  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  as a function of gas feed composition.

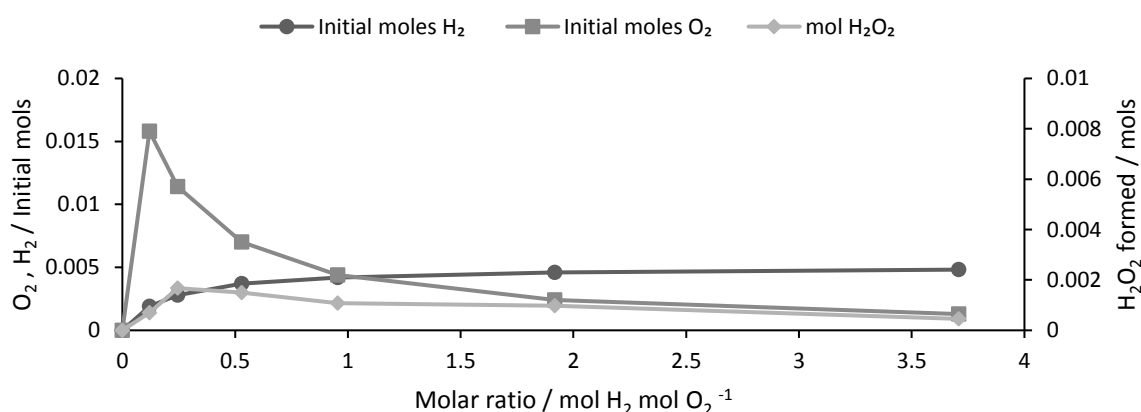
**Reaction conditions:** 2.5 wt. %Au – 2.5 wt. %Pd /  $\text{TiO}_2$  (0.01 g),  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  (0.05 g), total pressure 580 psi, 1200 rpm, 30 min, 5.6 g  $\text{CH}_3\text{OH}$  + 2.9 g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ), 2 °C.

It is observed that at lower  $\text{H}_2$  content ( $\text{H}_2$  :  $\text{O}_2$  ratio of 0.12) the observed  $\text{H}_2\text{O}_2$  concentration is particularly low, with a concentration of 0.28 wt. % reported when the  $\text{H}_2$  :  $\text{O}_2$  ratio is 0.12. This concentration of  $\text{H}_2\text{O}_2$  is twice that reported for the catalyst alone, under identical reaction conditions but a  $\text{H}_2$  :  $\text{O}_2$  ratio of 0.525<sup>24</sup>. Given the relative expense of  $\text{H}_2$  this may be of economic benefit to any large scale use of this reaction system for the direct synthesis of  $\text{H}_2\text{O}_2$ . By shifting the gas ratio slightly, to 0.25 it is possible to achieve extremely high concentrations of  $\text{H}_2\text{O}_2$ , with a total  $\text{H}_2\text{O}_2$  concentration of 0.67 wt. % reported. Increasing  $\text{H}_2$

content beyond this point is observed to result in a decrease in the total concentration of  $\text{H}_2\text{O}_2$  produced, to a minimum of 0.18 wt. %, when a  $\text{H}_2 : \text{O}_2$  ratio of 3.66 is employed.

The reaction gas consists of two components (5 %  $\text{H}_2 / \text{CO}_2$  and 25 %  $\text{O}_2 / \text{CO}_2$ ) as such as the  $\text{H}_2 : \text{O}_2$  ratio changes so does the molar fraction of  $\text{CO}_2$ . It has been previously shown that  $\text{CO}_2$ , when used as the diluent for the reactant gasses is able to promote  $\text{H}_2\text{O}_2$  selectivity through the formation of carbonic acid in the water-methanol solvent<sup>25</sup>, lowering the solvent pH and stabilising  $\text{H}_2\text{O}_2$ . Nevertheless, it can be presumed that the amount of  $\text{CO}_2$  introduced is high enough to lead to complete saturation of the water-methanol solvent ensuring that the pH of the solution is constant regardless of the  $\text{H}_2 : \text{O}_2$  ratio. It is observed in Figure 3.7 that the  $\text{CO}_2$  content does not vary to a great extent with increasing  $\text{O}_2$  content, as such the data in Figure 3.7 are likely to be representative of the effect of variation in the  $\text{H}_2 : \text{O}_2$  ratio and not  $\text{CO}_2$  content.

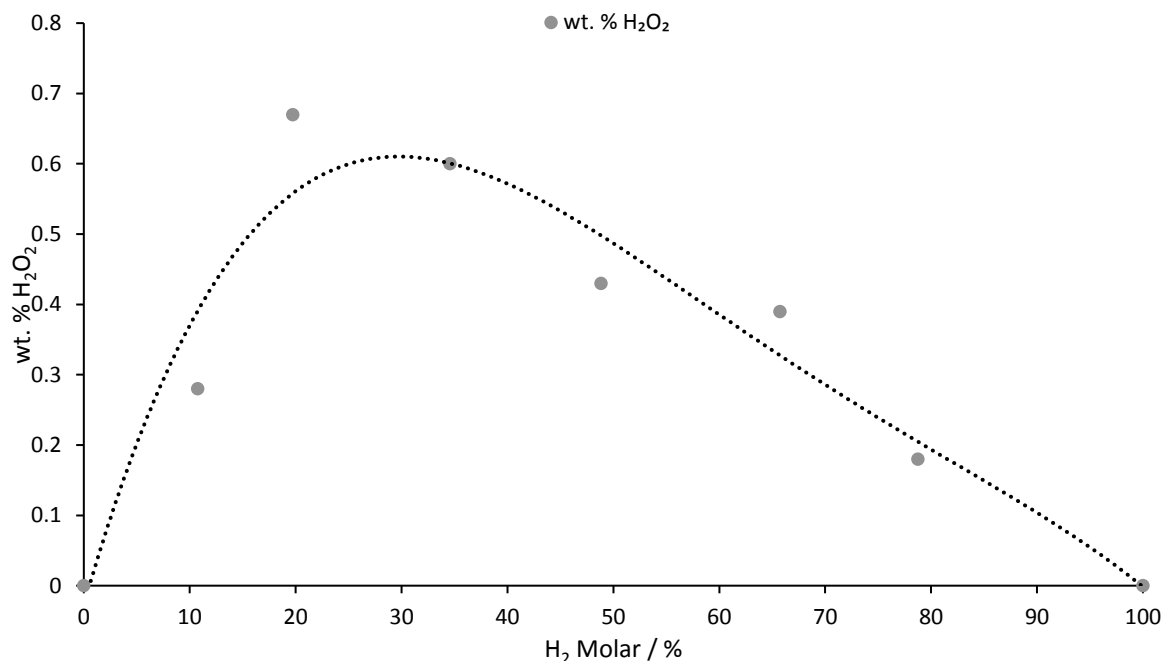
It may therefore be possible to explain the trend observed in Figure 3.7 in terms of limitation of reagent availability, in particular  $\text{H}_2$ . Figure 3.8 shows how the shape of the experimental curve seems to correlate to the limiting reagent ( $\text{H}_2$ ) concentration.



**Figure 3.8.** Comparison between total amount of moles  $\text{H}_2$  and  $\text{O}_2$  introduced to each experiment and  $\text{H}_2\text{O}_2$  produced for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  and  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$ .

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  (0.01 g),  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  (0.05 g), total pressure 580 psi, 1200 rpm, 30 min, 5.6 g  $\text{CH}_3\text{OH}$  + 2.9 g  $\text{H}_2\text{O}$  (66 Wt. %  $\text{CH}_3\text{OH}$ ), 2 °C.

For a simple model it may be expected that the synthesis of  $\text{H}_2\text{O}_2$  is equally dependent on the  $\text{H}_2 : \text{O}_2$  ratio as it is on the  $\text{O}_2 : \text{H}_2$  ratio. Figure 3.9 suggests that this is not the case.



**Figure 3.9.** wt. % H<sub>2</sub>O<sub>2</sub> produced for 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> and Cs<sub>0.1</sub>H<sub>2.9</sub>PW<sub>12</sub>O<sub>40</sub> as a function of reactant gas composition.

**Reaction conditions:** 2.5 wt. %Au – 2.5 wt. %Pd / TiO<sub>2</sub> (0.01 g), Cs<sub>0.1</sub>H<sub>2.9</sub>PW<sub>12</sub>O<sub>40</sub> (0.05 g), total pressure 580 psi, 1200 rpm, 30 min, 5.6 g CH<sub>3</sub>OH + 2.9 g H<sub>2</sub>O (66 wt. % CH<sub>3</sub>OH), 2 °C.

The shape of the curve in Figure 3.9 is not symmetrical, it is observed that greater partial pressures of H<sub>2</sub> leads to a marked decrease in the yield of H<sub>2</sub>O<sub>2</sub> in comparison to greater partial pressures of O<sub>2</sub>. This can be explained by considering the competing reactions that take place over the surface of the catalyst during the direct synthesis of H<sub>2</sub>O<sub>2</sub>, namely:

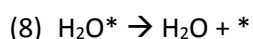
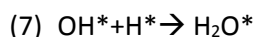
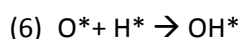
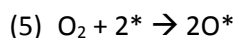
- Formation of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub>.
- Formation of H<sub>2</sub>O from H<sub>2</sub> and O<sub>2</sub> via combustion.
- Hydrogenation of H<sub>2</sub>O<sub>2</sub> by H<sub>2</sub>.
- Decomposition of H<sub>2</sub>O<sub>2</sub> to H<sub>2</sub>O.

It has been suggested by Ntainjua *et.al*<sup>26</sup>. that these reaction pathways share the same surface intermediates and the formation of H<sub>2</sub>O<sub>2</sub> occurs via the hydrogenation of O<sub>2</sub>. The following kinetic scheme has been proposed with this in mind<sup>26</sup>:

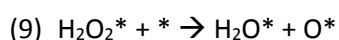
- (1)  $\text{H}_2 + 2^* \rightarrow 2 \text{H}^*$
- (2)  $\text{O}_2 + ^* \rightarrow \text{O}_2^*$
- (3)  $\text{H}^* + \text{O}_2^* \rightarrow \text{O}_2\text{H}^* + ^*$
- (4)  $\text{O}_2\text{H}^* + \text{H}^* \rightarrow \text{H}_2\text{O}_2^* + ^*$

Where \* denotes a vacant site.

It is therefore proposed that the formation of  $\text{H}_2\text{O}_2$  takes place via a twostep hydrogenation of adsorbed  $\text{O}_2$ . The undesired, competing reactions leading to the formation of  $\text{H}_2\text{O}$  are proposed to involve the dissociation of  $\text{O}_2$ :



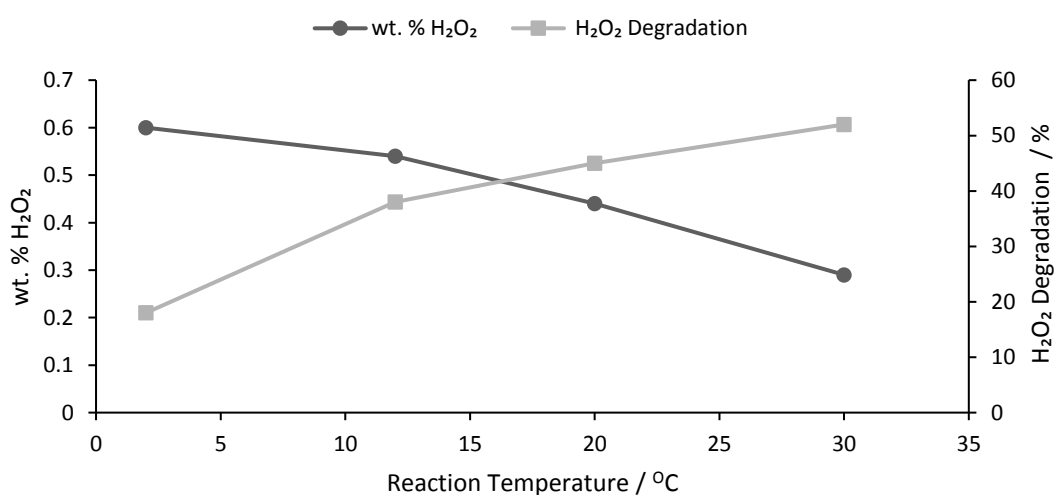
When two reaction sites are present in close proximity  $\text{H}_2\text{O}_2$  can dissociate in the following manner:



With this in mind it is possible to understand why at higher partial pressures of  $\text{H}_2$  the rate of  $\text{H}_2\text{O}_2$  degradation is much greater than the rate of  $\text{H}_2\text{O}_2$  synthesis, with an excess of  $\text{H}_2$  there is increased scavenging of  $\text{O}^*$  by atomic hydrogen. The contribution to  $\text{H}_2\text{O}_2$  degradation is likely to be greatest from hydrogenation rather than decomposition. It would be of interest to decouple the two pathways that contribute to  $\text{H}_2\text{O}_2$  degradation.

### 3.2.4.2. Effect of reaction temperature.

Reaction temperature was investigated while maintaining all other reaction conditions, the results of this experiment are shown in Figure 3.10.



**Figure 3.10.**  $\text{H}_2\text{O}_2$  concentration (wt. %) and  $\text{H}_2\text{O}_2$  degradation (%) for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  and  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  as a function of temperature.

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  (0.01 g),  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  (0.05 g), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 5.6 g  $\text{CH}_3\text{OH}$  + 2.9 g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ).

As can be observed in Figure 3.10 as reaction temperature increases the concentration of  $\text{H}_2\text{O}_2$  formed decreases with a corresponding increase in  $\text{H}_2\text{O}_2$  degradation. This is similar to the findings of Crole *et.al.*<sup>27</sup> who have investigated the effect of temperature on the direct synthesis of  $\text{H}_2\text{O}_2$  by 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  in a water only solvent.

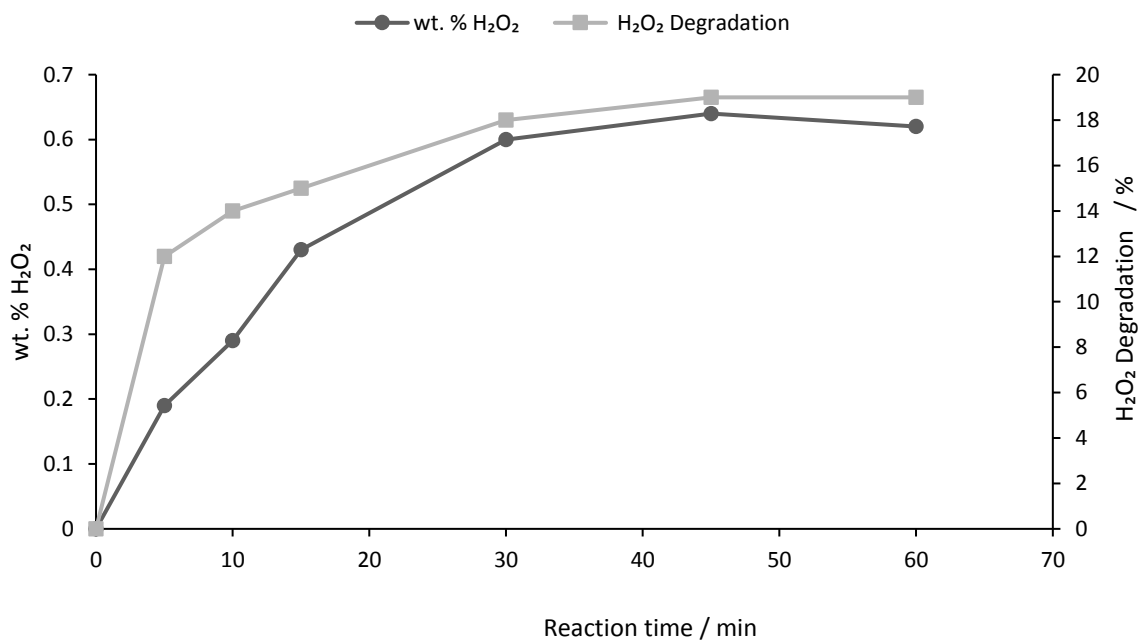
It is known that as temperature increases the solubility of  $\text{H}_2$  in methanol increases, conversely  $\text{H}_2$  solubility in water decreases with increasing temperature<sup>18</sup>. Furthermore  $\text{O}_2$  solubility in both water and methanol decreases with increasing temperature. It is therefore reasonable to propose that there is both a decrease in  $\text{H}_2\text{O}_2$  synthesis and an increase in the rate of subsequent  $\text{H}_2\text{O}_2$  hydrogenation, a significant component in  $\text{H}_2\text{O}_2$  degradation. This assumption was investigated and indeed it is shown that as temperature increases so does  $\text{H}_2\text{O}_2$  degradation. However the individual components of  $\text{H}_2\text{O}_2$  degradation (decomposition and hydrogenation) have not been decoupled and therefore it is not possible to definitively state if the increase in degradation is due to decomposition or hydrogenation, or both.

The optimal temperature for this catalytic system is found to be 2 °C, where  $\text{H}_2\text{O}_2$  concentration is reported to be greatest at 0.6 wt. % and the rate of degradation is at its lowest at 18 %. Although it should be noted that even at elevated temperatures high catalytic activity is still observed, indeed at 30 °C a  $\text{H}_2\text{O}_2$  concentration of 0.29 wt. % is observed, even though the extent of  $\text{H}_2\text{O}_2$  degradation is over 2.5 times that observed at 2 °C. The concentration of  $\text{H}_2\text{O}_2$  synthesised is in excess of twice that reported for the 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$ , under conditions optimised for this catalyst (0.128 wt.%). It is reasonable to assume that the observed rate of  $\text{H}_2\text{O}_2$  synthesis, as with all systems studied for the direct synthesis of  $\text{H}_2\text{O}_2$ , is lower than the true rate as at elevated temperatures the degradation of  $\text{H}_2\text{O}_2$  becomes prevalent and as such not all the  $\text{H}_2\text{O}_2$  formed is available at the end of the reaction.

This work is in finding with Crole *et.al.*<sup>27</sup> who have investigated 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  in a  $\text{H}_2\text{O}$  only solvent under a batch reaction conditions. In addition to this work Freakley *et.al.*<sup>14</sup> have investigated 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  in a  $\text{H}_2\text{O}$ -MeOH solvent system, in a flow reactor. It is reported that increasing reaction temperature from 2 to 30 °C results in a decrease in productivity and this is ascribed to a decrease in the solubility of  $\text{O}_2$  in both solvent components<sup>27</sup>. Furthermore it is reported that the solubility of  $\text{H}_2$  increases in methanol by approximately 30 % as temperature is raised from 2 to 30 °C, resulting in an increase in the rate of  $\text{H}_2\text{O}_2$  hydrogenation and a decrease in  $\text{H}_2\text{O}_2$  selectivity.

### 3.2.4.3. The effect of reaction time.

Figure 3.11 shows the effect of reaction time on the concentration of  $\text{H}_2\text{O}_2$  formed and the extent of  $\text{H}_2\text{O}_2$  degradation. Reactions were performed for systematically varied durations to study the effect of time on the amount of  $\text{H}_2\text{O}_2$  formed and subsequently degraded. Separate reactions were performed as sampling from a single reaction in a time on line process would affect the reaction dynamics.



**Figure 3.11.**  $\text{H}_2\text{O}_2$  concentration (wt. %) and  $\text{H}_2\text{O}_2$  degradation (%) for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  and  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  as a function of time.

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  (0.01 g),  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  (0.05 g), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 2 °C, 5.6 g  $\text{CH}_3\text{OH}$  + 2.9 g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ).

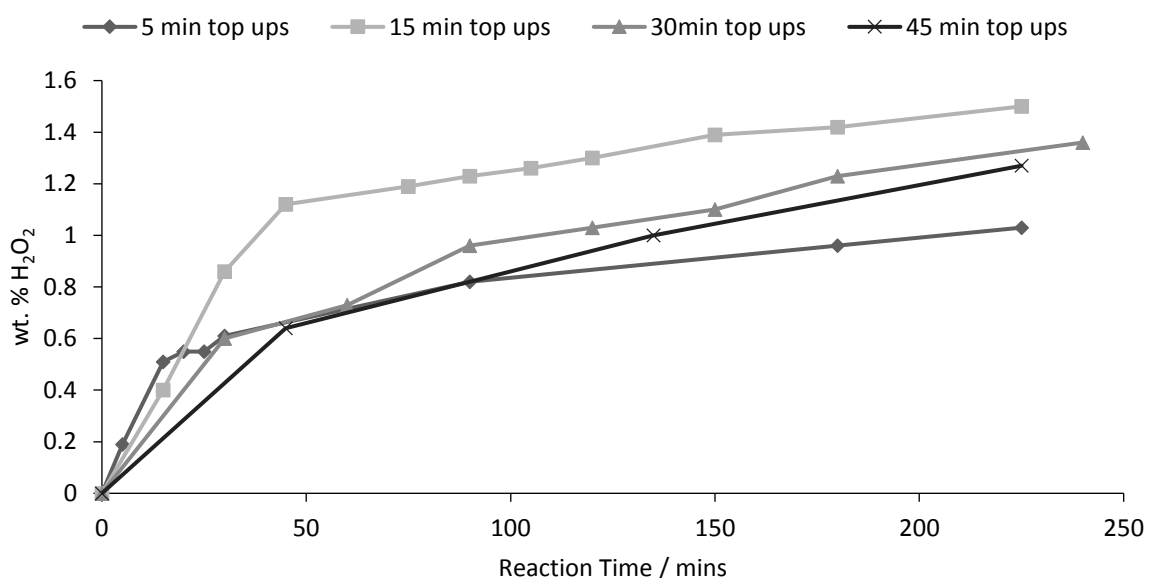
Initially, as reaction time increases so does the concentration of  $\text{H}_2\text{O}_2$ , to 0.19 wt. % at a reaction time of 5 minutes. Beyond this point  $\text{H}_2\text{O}_2$  concentration increases to a maximum of 0.64 wt. % after 45 minutes. It may be expected that  $\text{H}_2\text{O}_2$  concentration would increase continuously with time, however as time increases the availability of both  $\text{H}_2$  and  $\text{O}_2$  in the system decreases; the system is then limited by the availability of reactants.

The degradation of  $\text{H}_2\text{O}_2$  is observed to increase sharply with reaction time; until 30 minutes where degradation is reported to be 18 %. Beyond this point the rate of degradation plateaus, as with the  $\text{H}_2\text{O}_2$  yield, this is ascribed to decreasing availability of reactant gasses.

Both  $\text{H}_2\text{O}_2$  degradation and  $\text{H}_2\text{O}_2$  yield suggest that after a reaction time of 30 minutes the reaction becomes limited by the availability of reactants, it can be observed that at a time of 30 minutes  $\text{H}_2\text{O}_2$  concentration is 0.6 wt% while after 30 minutes  $\text{H}_2\text{O}_2$  concentration

plateaus. This is supported by data in Table 3.2, which shows that at a reaction time of 30 min  $\text{H}_2$  conversion 69 %. However, it is possible that after 30 minutes the catalyst has become deactivated and this would explain the lack of variation in both the  $\text{H}_2\text{O}_2$  yield and the extent of  $\text{H}_2\text{O}_2$  degradation.

In an attempt to determine if at a reaction time of 30 minutes the catalyst has become deactivated or the system operates inside of mass transport limitation it was decided to investigate ‘top up’ reactions, where the reactant gas was replaced periodically. The length of time between gas replacements was studied in order to determine if this factor affects catalytic activity towards the direct synthesis of  $\text{H}_2\text{O}_2$ . A range of gas replacement times were chosen, ranging from 5 minute intervals to standard reaction length time, 30 minute intervals, to longer reaction times, 45 minute intervals, and the results are shown in Figure 3.12.



**Figure 3.12.**  $\text{H}_2\text{O}_2$  concentration (wt. %) for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  and  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  as a function of reaction gas replacement.

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  (0.01 g),  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  (0.05 g), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 2 °C, 5.6 g  $\text{CH}_3\text{OH}$  + 2.9 g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ).

It is observed that when replacement of the reactant gas occurs every 5 minutes, to give a total reaction time of 30 minutes (6 gas charges) the total  $\text{H}_2\text{O}_2$  concentration is very similar to that observed when one 30 minute reaction is investigated, with no gas replacements, 0.6 and 0.61 wt. %. Again this is very similar to the  $\text{H}_2\text{O}_2$  concentration reported for a 45 minute reaction, with one gas charge, with  $\text{H}_2\text{O}_2$  yield reported to be 0.64 wt.%. Interestingly when the reactant gas is replaced at 15 minute intervals, to give a total reaction time of 30 minutes

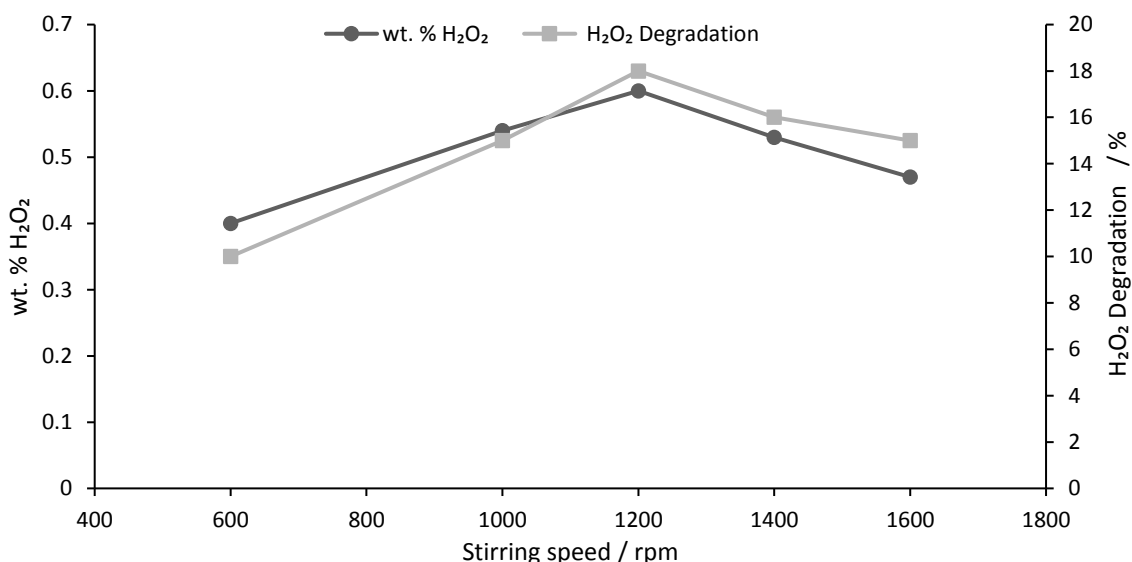
(2 gas charges) the  $\text{H}_2\text{O}_2$  concentration is much higher than gas replacements at either 5, 30 or 45 minute intervals. Indeed  $\text{H}_2\text{O}_2$  concentration is reported to be 0.86 wt. %.

It is suggested that at shorter reaction times the reactant gas is unable to fully diffuse to the catalyst surface and so the reaction is limited by reactant availability. It is observed in Figure 3.12 that after 30 minutes, if the reactant gas is not replaced the formation of  $\text{H}_2\text{O}_2$  becomes mass transport limited. As such when longer gas replacement times, 30 and 45 minutes, are employed the reaction becomes limited by the availability of  $\text{H}_2$  or  $\text{O}_2$ . However using a replacement time of 15 minutes ensures that both significant amounts of  $\text{H}_2$  and  $\text{O}_2$  are able to diffuse to the catalyst surface and the reaction remains outside of mass transport limitation.

It would be of great interest to investigate catalyst activity while maintaining reactant gas pressure, this would allow the system to be studied in a manner more similar to that likely used on a larger industrial scale and allow for the investigation of catalyst stability over time.

#### 3.2.4.4. The effect of stirring speed.

Figure 3.13 shows the effect of the stirring speed on  $\text{H}_2\text{O}_2$  yield and  $\text{H}_2\text{O}_2$  degradation.



**Figure 3.13.**  $\text{H}_2\text{O}_2$  concentration (wt. %) and  $\text{H}_2\text{O}_2$  degradation (%) for 2.5 wt. % Au – 2.5 wt. % Pd/ $\text{TiO}_2$  and  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  as a function of stirring speed.

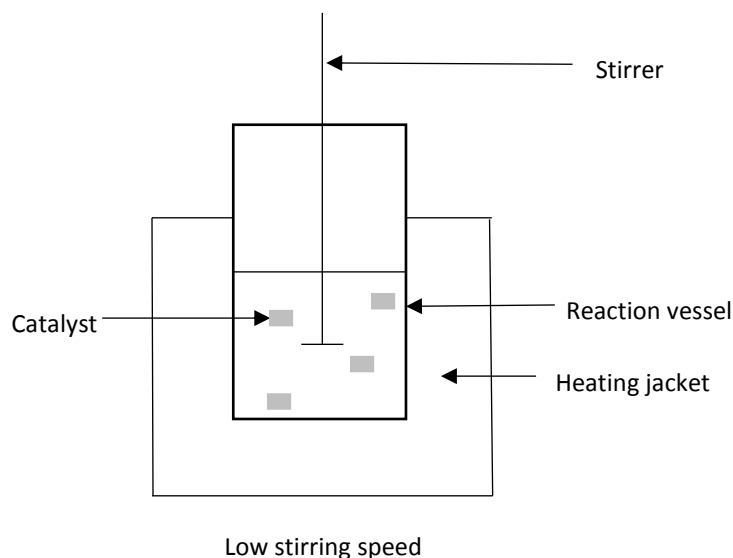
**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  (0.01 g),  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  (0.05 g), total pressure 580 psi,  $\text{H}_2/\text{O}_2=0.525$ , 2 °C, 30 min, 5.6 g  $\text{CH}_3\text{OH}$  + 2.9 g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ).

It could be assumed that an increase in stirring speed would be beneficial to the yield of  $\text{H}_2\text{O}_2$ . It is likely that increasing stirring speed would result in an improvement in mass transfer of reactants to the catalyst. Likewise it would be expected that at lower stirring speeds that

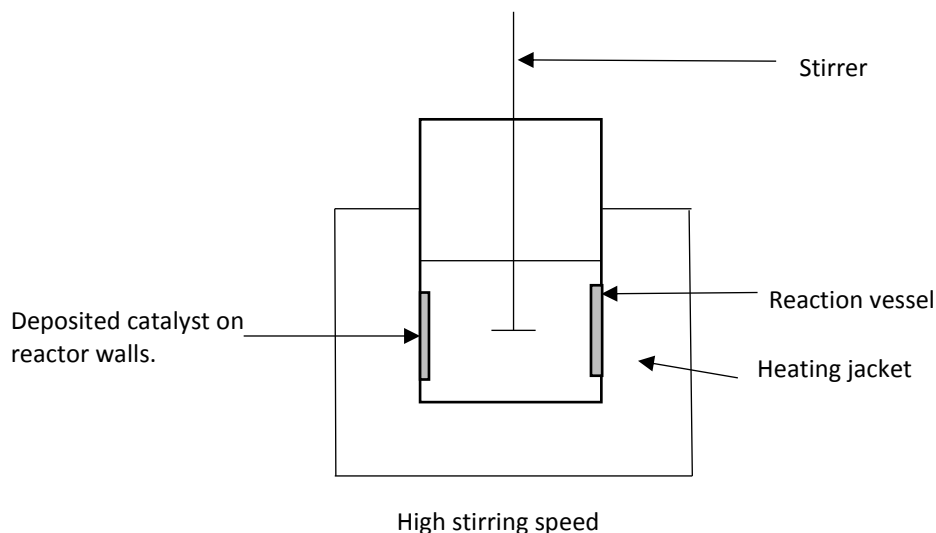


mass transfer of reactants to the catalyst active sites would be reduced and conversion to the product,  $\text{H}_2\text{O}_2$ , would be less than at higher speeds. The data shows that at stirring speeds below 1200 rpm,  $\text{H}_2\text{O}_2$  concentration is considerably lower than that observed at 1200 rpm, with  $\text{H}_2\text{O}_2$  yield observed to be 0.47 wt. % at a stirring speed of 600 rpm. While at a stirring speed of 1200 rpm  $\text{H}_2\text{O}_2$  yield is reported to be 0.6 wt. %.

As with  $\text{H}_2\text{O}_2$  yield,  $\text{H}_2\text{O}_2$  degradation is observed to reach a maxima at a stirring speed of 1200, with a degradation of 18 % reported. When increasing stirring speed beyond 1200 rpm a decrease in  $\text{H}_2\text{O}_2$  degradation, to 15 % is observed. It is suggested that, as both overall  $\text{H}_2\text{O}_2$  yield and  $\text{H}_2\text{O}_2$  degradation decreases beyond a stirring speed of 1200 rpm the reactants are unable to reach the active sites present on the catalyst responsible for these reaction pathways. As such this leads to a reduction in both the rate of  $\text{H}_2\text{O}_2$  synthesis and subsequent degradation. It is possible that at higher stirring speeds the catalyst is forced on to the autoclave liner and so the number of catalytic sites available to catalyse either the synthesis or degradation of  $\text{H}_2\text{O}_2$  decreases, as outlined in Figures 3.14 and 3.15.



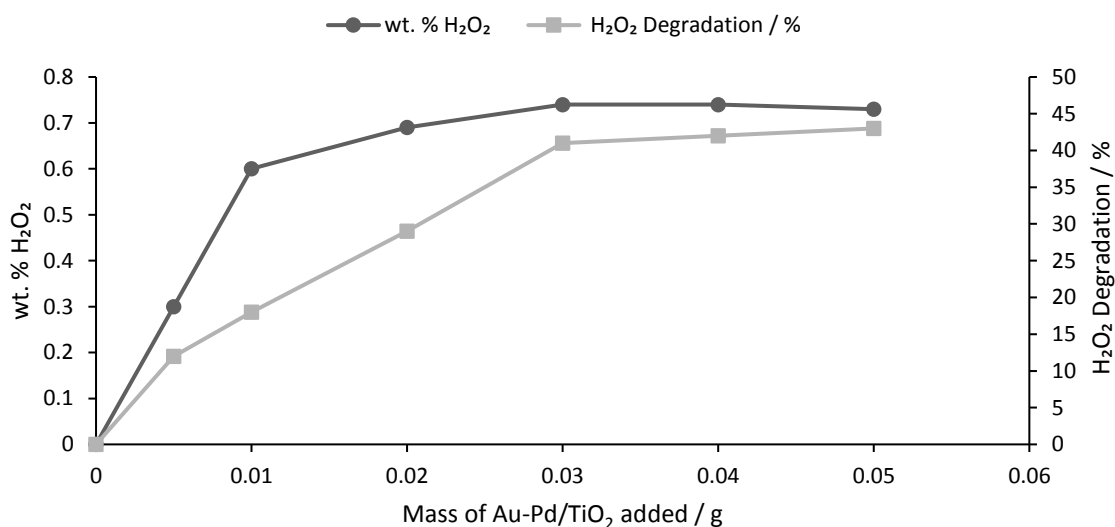
**Figure 3.14.** The effect of low reactor speed on catalyst distribution in a sealed autoclave.



**Figure 3.15.** The effect of high reactor speed on catalyst distribution in a sealed autoclave.

### 3.2.4.5. The effect of catalyst mass.

Figure 3.16 show the effect of the catalyst mass on the concentration of  $\text{H}_2\text{O}_2$  and its subsequent degradation.



**Figure 3.16.**  $\text{H}_2\text{O}_2$  concentration (wt. %) and  $\text{H}_2\text{O}_2$  degradation (%) for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  and  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  as a function of 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  loading.

**Reaction conditions:**  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  (0.05 g), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 5.6 g  $\text{CH}_3\text{OH} + 2.9$  g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ), 2 °C.

It can be seen that increasing the mass of the 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst increases the yield of  $\text{H}_2\text{O}_2$ , to a maximum of 0.74 wt. % when 0.03 g of catalyst is utilised. Beyond this point  $\text{H}_2\text{O}_2$  concentration reaches a plateau. This is in agreement with the work conducted by Edwards *et.al.*<sup>23</sup> who investigated the 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst under identical conditions, but in the absence of the  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  additive. It should be

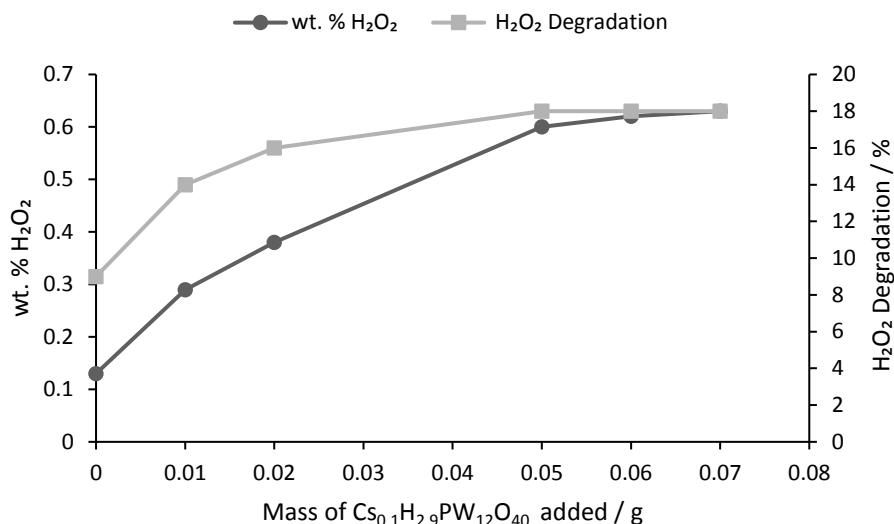
noted that Edwards and co-workers report a maximum  $\text{H}_2\text{O}_2$  concentration of 0.32 Wt. % when the catalyst is used solely. The addition of the  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  additive is reported to increase the yield of  $\text{H}_2\text{O}_2$  to 0.74 Wt. %, more than twice that reported by Edwards *et.al*<sup>24</sup>.

It is observed that by increasing catalyst mass it is possible to increase  $\text{H}_2\text{O}_2$  concentration, to a maximum of 0.74 wt. % when 0.03 g of the catalyst is utilised. Beyond this point, further addition of catalyst does not result in an increase in  $\text{H}_2\text{O}_2$  concentration.

As discussed above  $\text{H}_2\text{O}_2$  concentration plateaus beyond the addition of 0.03 g of Au-Pd /  $\text{TiO}_2$ . It could be assumed that this may be due to the rate of either one or both  $\text{H}_2\text{O}_2$  degradation pathways becoming greater than the rate of  $\text{H}_2\text{O}_2$  synthesis. However investigation of the extent of  $\text{H}_2\text{O}_2$  degradation with varied catalyst loadings shows a similar trend to that observed for  $\text{H}_2\text{O}_2$  yield, with  $\text{H}_2\text{O}_2$  degradation reaching a plateau as catalyst mass is increased beyond 0.03 g. It is suggested that this is due to limited availability of the reactants ( $\text{H}_2$  and  $\text{O}_2$ ). The system is now limited by mass transfer. Further addition of catalyst does not result in an increase in  $\text{H}_2\text{O}_2$  yield. Furthermore it is suggested that when utilising greater masses of catalyst the high stirring speed forces a greater proportion of the catalyst onto the walls of the reactor, preventing access to active sites on the catalyst, in a manner similar to that described in Section 3.2.4.4. There may also be greater agglomeration of catalyst as total catalyst mass increases, which in turn reduces the availability of sites active towards the degradation and synthesis of  $\text{H}_2\text{O}_2$ .

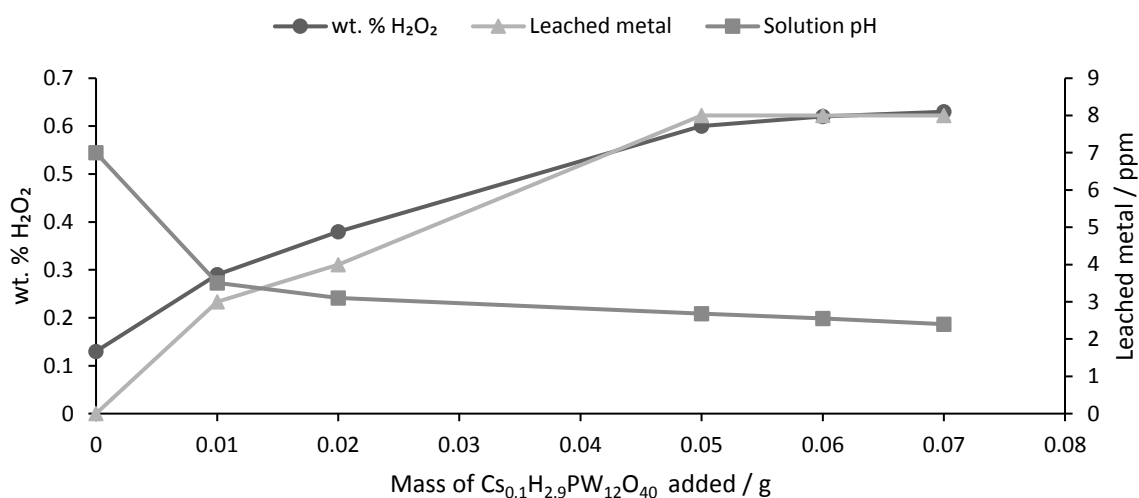
#### 3.2.4.6. Effect of $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$ mass.

Figure 3.17 shows the effect of increasing the mass of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  used in addition to 0.01 g of 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  for the direct synthesis and subsequent degradation of  $\text{H}_2\text{O}_2$ . The effect of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  content on the leaching of metals from the support during the direct synthesis reaction is also observed in Figure 3.18 as is the pH of the reaction solution prior to reaction.



**Figure 3.17.**  $\text{H}_2\text{O}_2$  concentration (wt. %) and  $\text{H}_2\text{O}_2$  degradation (%) for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  and  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  as a function of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  loading.

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  (0.01g), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 5.6 g  $\text{CH}_3\text{OH}$  + 2.9 g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ), 2 °C.



**Figure 3.18.**  $\text{H}_2\text{O}_2$  concentration (wt. %), concentration of leached metal (ppm) and reaction solution pH for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  and  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  as a function of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  loading.

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  (0.01g), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 5.6 g  $\text{CH}_3\text{OH}$  + 2.9 g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ), 2 °C.

It is observed, in Figure 3.17, that the addition of increasing amounts of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  leads to an increase in the concentration of  $\text{H}_2\text{O}_2$ . Yield of  $\text{H}_2\text{O}_2$  increases from 0.13 wt. % when only the 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst is present to 0.6 wt. % when 0.05 g of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  is utilised in addition to the catalyst. Beyond this point further addition of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  results in a very limited improvement in concentration of  $\text{H}_2\text{O}_2$ , to a

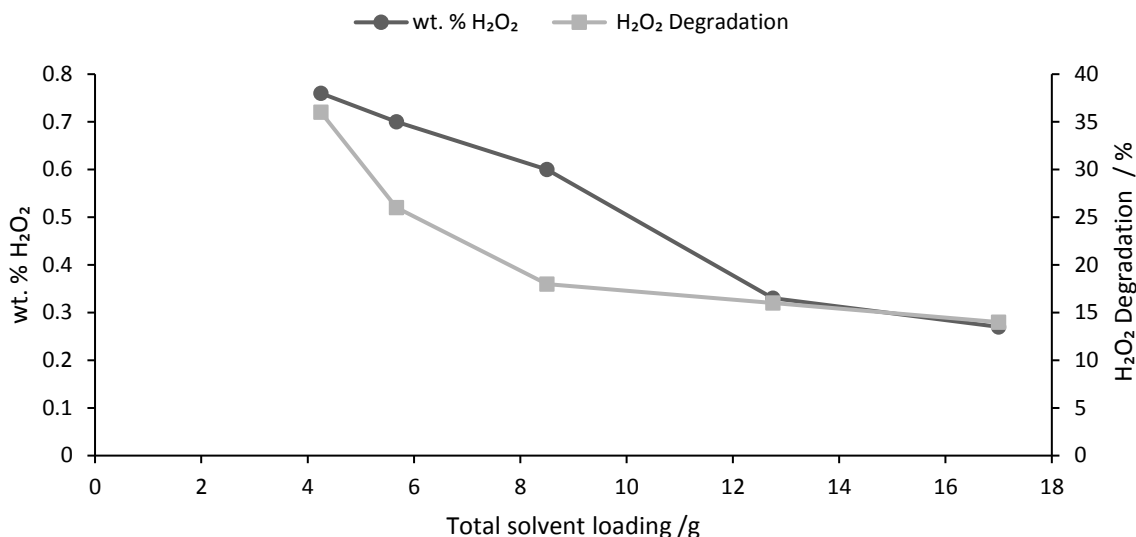
maximum of 0.63 wt. % when 0.07 g of the additive is used. This can be related to the pH of the reaction solution, observed in Figure 3.18. It is observed that the pH of the reaction solution decreases dramatically with the addition of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$ , from a pH of 7 when only the catalyst is present to 3.51 when 0.01 g of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  is introduced also. This corresponds to an improvement in  $\text{H}_2\text{O}_2$  yield, from 0.13 to 0.29 wt. %. Further addition of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  decreases the pH of the reaction solution slightly to 2.4 when 0.07 g of the additive is utilised, with a  $\text{H}_2\text{O}_2$  concentration of 0.63 wt. % reported. It has previously been reported that acidic reaction conditions are favourable towards  $\text{H}_2\text{O}_2$  formation, with a decrease in  $\text{H}_2\text{O}_2$  degradation reported when using acidic conditions<sup>7 8 28</sup>. It would therefore be reasonable to suggest that the improvement in  $\text{H}_2\text{O}_2$  yield is related to a decrease in the pH of the reaction solution.

However as the mass of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  added increases so does the degradation of  $\text{H}_2\text{O}_2$ , from 10 % when no  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  is present to 18 % when 0.05 g of the additive is used. Increasing the mass of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  added further to 0.07g does not lead to an increase in the rate of  $\text{H}_2\text{O}_2$  degradation. It has previously been shown in Table 3.7 that Cs can contribute to the degradation of  $\text{H}_2\text{O}_2$  and that as Cs content increases so does the degradation of  $\text{H}_2\text{O}_2$ . Furthermore, investigation into the stability of Cs-exchanged tungstophosphoric acid, Table 3.3, shows that a Cs loading equal to  $\text{Cs}_{0.1}$  is not sufficient to produce a stable material, as inferred from the high concentration of W present in the reaction solution, 1723 ppm when  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  is utilised in comparison to 1834 ppm when the non-substituted  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  is utilised. It is suggested that the increasing Cs content, as more  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  is added, within the solvent system is the cause for the increase in degradation of  $\text{H}_2\text{O}_2$ . This further correlates with the data observed in Table 3.1, which highlights the ability of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  to degrade  $\text{H}_2\text{O}_2$ .

It is observed in Figure 3.18 that as the mass of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  added increases the concentration of leached Pd increases, from 0 ppm when the catalyst is used alone to a maximum of 9 ppm when 0.07g of  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  is utilised. Investigation into the ability of free Pd towards the direct synthesis of  $\text{H}_2\text{O}_2$  has been conducted in Table 3.5. It is shown that there is some activity towards the direct synthesis of  $\text{H}_2\text{O}_2$ , with catalytic productivity reported as  $19 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$  corresponding to a  $\text{H}_2\text{O}_2$  yield of 0.039 wt. %. However it is suggested that the contribution towards  $\text{H}_2\text{O}_2$  synthesis from the leached Pd is minor and the increased  $\text{H}_2\text{O}_2$  yield is due to the decrease in reaction solution pH and subsequent improvement in  $\text{H}_2\text{O}_2$  stability.

### 3.2.4.7. Effect of solvent mass.

The role of solvent mass on the direct synthesis and degradation of  $\text{H}_2\text{O}_2$  was investigated, while maintaining all other reaction conditions, the results of this investigation are observed, in Figure 3.19.



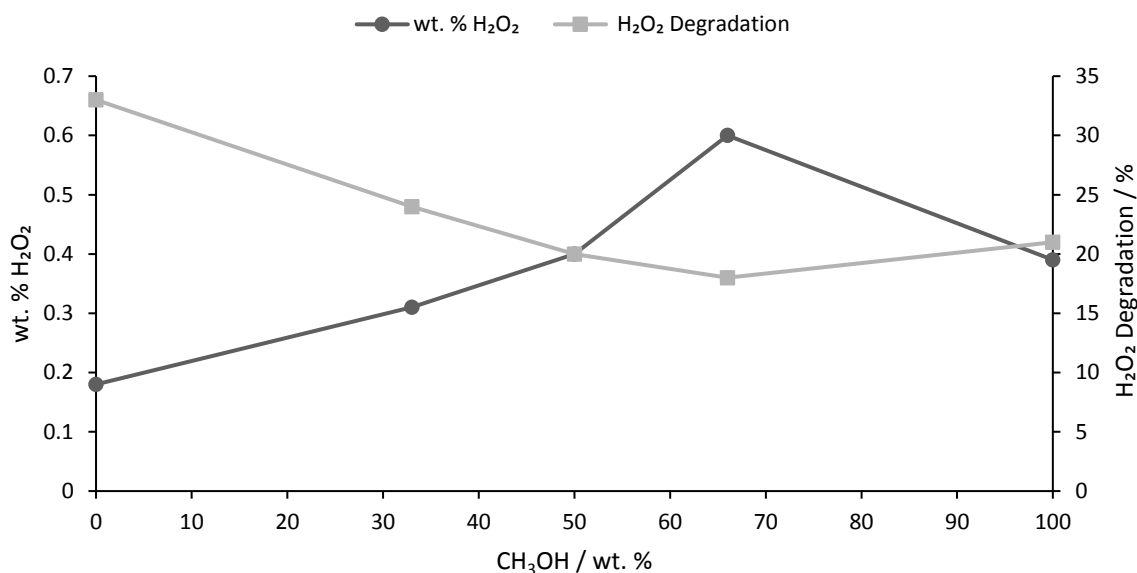
**Figure 3.19.**  $\text{H}_2\text{O}_2$  Productivity and  $\text{H}_2\text{O}_2$  wt. % for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  and  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  as a function of solvent loading.

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  (0.01 g),  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  (0.05 g), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 66 wt. %  $\text{CH}_3\text{OH}$ , 2 °C.

It is observed that increasing total solvent loading results in a decrease in total concentration of  $\text{H}_2\text{O}_2$ , with  $\text{H}_2\text{O}_2$  concentration decreasing from 0.76 to 0.27 wt. % as total solvent loading increases from 4.25 to 17 g, while maintaining the ratio of water to methanol at 1 : 2. As with  $\text{H}_2\text{O}_2$  yield  $\text{H}_2\text{O}_2$  degradation decreases with total solvent loading, from a maxima of 36 % when 4.5 g of solvent to a minima of 14 % when 17 g of solvent is utilised. It is suggested that reactant availability may be responsible for the loss in activity towards. As total solvent loading increases so the available head space within the reactor decreases. This means that there is less  $\text{H}_2$  and  $\text{O}_2$  available for the synthesis of  $\text{H}_2\text{O}_2$  and less  $\text{H}_2$  present for the degradation of  $\text{H}_2\text{O}_2$ . Furthermore it is suggested that increasing solvent loading results in a greater diffusion pathway from the boundary interphase between the gas – solvent boundary to the surface of the catalyst.

#### 3.2.4.8. Effect of H<sub>2</sub>O / CH<sub>3</sub>OH ratio.

The effect that the ratio of methanol to water has on the direct synthesis and degradation of H<sub>2</sub>O<sub>2</sub> was investigated, while keeping the total amount of solvent constant at 8.5 g. The results are shown in Figure 3.20.



**Figure 3.20.** H<sub>2</sub>O<sub>2</sub> Productivity and H<sub>2</sub>O<sub>2</sub> wt. % for 2.5 Wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> and Cs<sub>0.1</sub>H<sub>2.9</sub>PW<sub>12</sub>O<sub>40</sub> as a function of solvent composition.

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> (0.01 g), Cs<sub>0.1</sub>H<sub>2.9</sub>PW<sub>12</sub>O<sub>40</sub> (0.05 g), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 66 wt. % CH<sub>3</sub>OH, 2 °C.

It is observed that as total methanol content increases to 66 wt. % catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis increases, with H<sub>2</sub>O<sub>2</sub> concentration increasing to a maxima of 0.6 wt. %, when a water : methanol ratio of 1 : 2 is employed. Beyond this point H<sub>2</sub>O<sub>2</sub> yield decreases to 0.39 wt. %, in a methanol only solvent and this can be ascribed to the improved solubility of H<sub>2</sub> in methanol in comparison to water. This is a similar observation to that reported by Crole *et.al.*<sup>27</sup> who have investigated the effect of solvent composition under similar reaction conditions, using a AuPd / TiO<sub>2</sub> catalyst. The decrease in H<sub>2</sub>O<sub>2</sub> synthesis beyond a total methanol content of 66 wt. % is ascribed to the lower solubility of O<sub>2</sub> in methanol. As the solvent system becomes increasingly methanol rich the availability of O<sub>2</sub> decreases and in turn so does the rate of H<sub>2</sub>O<sub>2</sub> formation.

Interestingly, the extent of H<sub>2</sub>O<sub>2</sub> degradation decreases as methanol content increases, from 33 % when a water only solvent is employed to 18 % when a methanol-water solvent is used in a ratio of 2 : 1. It would be assumed that the rate of hydrogenation would increase as the

system becomes more methanol rich and as such the total amount of H<sub>2</sub>O<sub>2</sub> degradation would increase. Indeed, Crole *et.al.*<sup>27</sup> have shown that as the solvent becomes more methanol rich the rate of H<sub>2</sub>O<sub>2</sub> hydrogenation increase, however it is also reported that rate of H<sub>2</sub>O<sub>2</sub> decomposition decreases drastically. It would therefore be of great interest to decouple the two degradation pathways and determine if a similar trend is observed; where hydrogenation increases but decomposition decreases as the solvent becomes increasingly methanol rich. Beyond a 2 : 1 ratio of methanol : water there is a slight increase in the rate of H<sub>2</sub>O<sub>2</sub> degradation to 20 % in a pure methanol solvent.

It is known that H<sub>2</sub>O<sub>2</sub> stability is improved by the presence of acidic reaction conditions<sup>18</sup>, and that the use of CO<sub>2</sub> as the reactant gas diluent has been shown to result in the formation of carbonic acid, improving H<sub>2</sub>O<sub>2</sub> selectivity<sup>25</sup>. It is known that CO<sub>2</sub> has greater solubility in methanol than H<sub>2</sub>O<sup>29</sup> and so there may be greater stabilisation of H<sub>2</sub>O<sub>2</sub> as the solvent system becomes more methanol rich, due to increased formation of carbonic acid. However as water content decreases so the extent of H<sub>2</sub>O<sub>2</sub> degradation increases. As the presence of water is required for the formation of carbonic acid and subsequent stabilisation of H<sub>2</sub>O<sub>2</sub> it is possible that when using a methanol only solvent there is no stabilisation of H<sub>2</sub>O<sub>2</sub> from carbonic acid and as such H<sub>2</sub>O<sub>2</sub> degradation increases.

Previous work by Edwards *et.al.*<sup>30</sup> investigating Au-Pd/ TiO<sub>2</sub> in a water-methanol solvent system has reported that a maximum catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis is observed when a water : methanol ratio of 1 : 4 is employed, beyond this ratio catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis decreases drastically, from 90 to 15 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> as the water : methanol ratio is increased to 1 : 4.5. In comparison when AuPd / TiO<sub>2</sub> is utilised in addition to Cs<sub>0.1</sub>H<sub>2.9</sub>PW<sub>12</sub>O<sub>40</sub> it has been shown, in Figure 3.20, that a greater yield of H<sub>2</sub>O<sub>2</sub> can be achieved when using a water methanol ratio of 1 : 2.

It would therefore be of interest to better optimise the solvent composition for the 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> – Cs<sub>0.1</sub>H<sub>2.9</sub>PW<sub>12</sub>O<sub>40</sub> system to determine if an improvement in H<sub>2</sub>O<sub>2</sub> yield can be achieved.

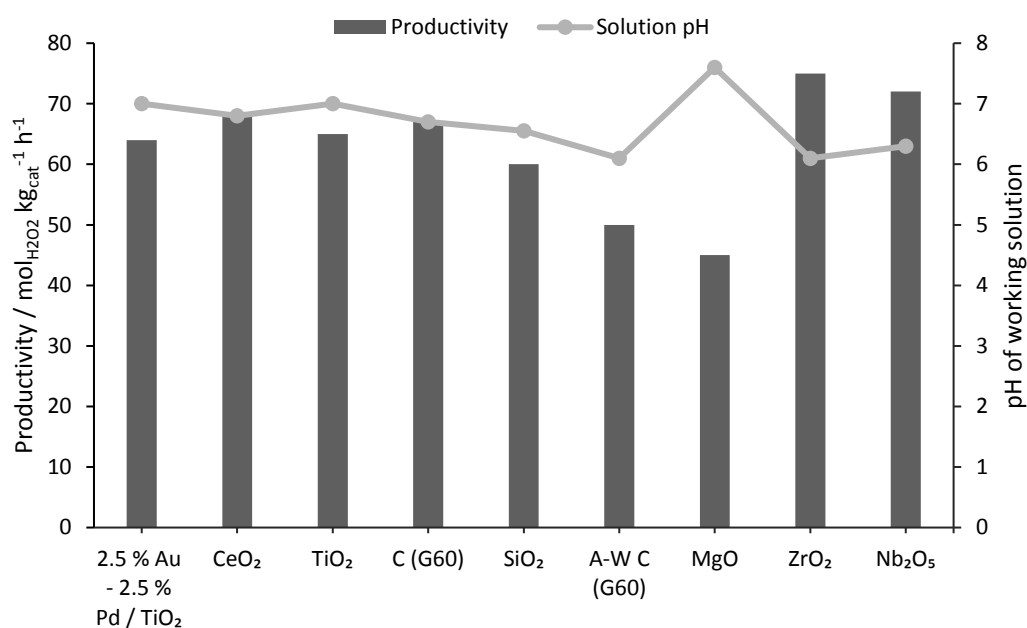
#### 3.2.5.1. Variation in pH of the water-methanol working solution using common supports as an additive to 2.5 Wt. % Au – 2.5 Wt. % Pd / TiO<sub>2</sub>

It has previously been shown (Table 3.4) that the addition of Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> salts alter the pH of the reaction solution prior to reaction, with decreasing Cs incorporation resulting in a more acidic reaction solution. It can be seen that there is a strong relationship between the



pH of the reaction solution and catalytic productivity. The addition of the  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  (0.05 g) lowers the pH from 7.0, when only 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  is present in the solution to 2.68 when the additive is used in conjunction with the catalyst. This coincides with an increase in catalytic activity towards  $\text{H}_2\text{O}_2$  synthesis, from  $64 \text{ mol}_{\text{H}_2\text{O}_2}\text{kg}_{\text{cat}}^{-1}\text{h}^{-1}$  for the 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst in the absence of the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salt to  $299 \text{ mol}_{\text{H}_2\text{O}_2}\text{kg}_{\text{cat}}^{-1}\text{h}^{-1}$  when the catalyst is used in addition to  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$ . As Cs incorporation increases the promotional effect towards  $\text{H}_2\text{O}_2$  synthesis decreases, to a minimum of  $86 \text{ mol}_{\text{H}_2\text{O}_2}\text{kg}_{\text{cat}}^{-1}\text{h}^{-1}$  when  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$  is utilised as an additive.

Furthermore Hutchings and workers have shown that the utilisation of acidic supports such as  $\text{SiO}_2$  and carbon produces a catalyst that is more active in the direct synthesis of  $\text{H}_2\text{O}_2$  than those where a basic support such as  $\text{MgO}$  is used<sup>31</sup>. For catalysts using supports with a lower isoelectric point, selectivity towards  $\text{H}_2\text{O}_2$  is greater and the activity towards the subsequent hydrogenation and decomposition reactions are lower<sup>32</sup>. With this in mind it was decided to investigate the ability of common supports to promote the activity of 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  towards  $\text{H}_2\text{O}_2$  synthesis with the results shown in Figure 3.21.



**Figure 3.21.**  $\text{H}_2\text{O}_2$  Productivity and pH of reaction solution for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  used in addition to common supports.

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  (0.01 g), Support (0.05 g), total pressure 580 psi,  $\text{H}_2/\text{O}_2=0.525$ , 1200 rpm, 30 min, 5.6 g  $\text{CH}_3\text{OH}$  + 2.9 g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ), 2 °C.

A correlation between catalytic activity and the pH of the reaction solution pH, prior to reaction, can be observed (Figure 3.21). An increase in catalytic activity can be reported as the reaction solution becomes more acidic. The addition of  $\text{ZrO}_2$  and  $\text{Nb}_2\text{O}_5$  (0.05 g) are

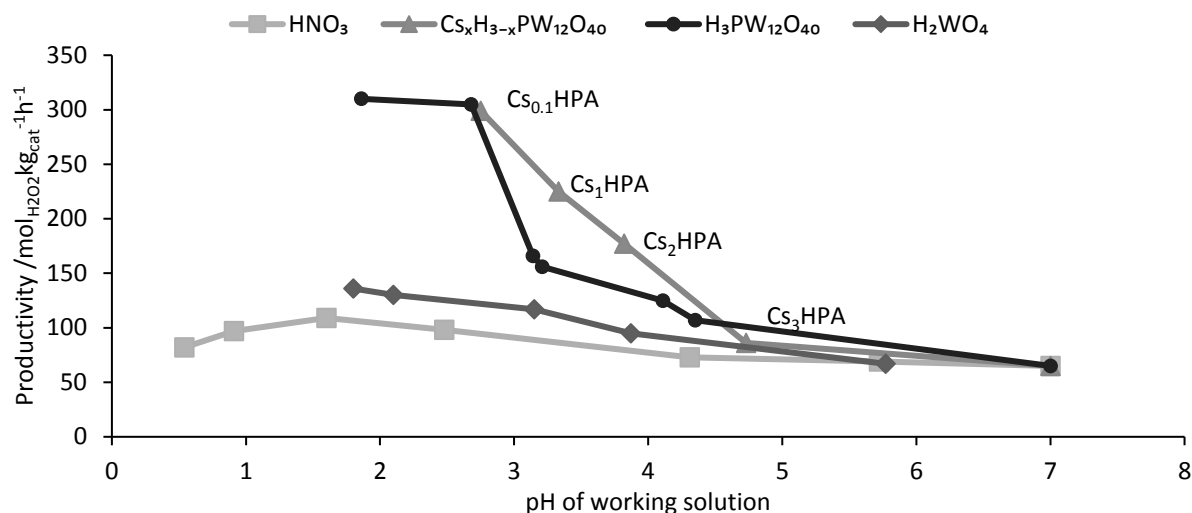
observed to lead to an increase in catalytic activity to 75 and 72  $\text{mol}_{\text{H}_2\text{O}_2}\text{kg}_{\text{cat}}^{-1}\text{h}^{-1}$  when  $\text{ZrO}_2$  and  $\text{Nb}_2\text{O}_5$  are used respectively as an additive for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$ . However the improvement in catalytic activity is minimal, especially compared to the increase observed when  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts are utilised as additives for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$ , regardless of Cs incorporation.

Furthermore it is noted that the use of MgO in addition to the 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst results in a significant increase in reaction solution pH, to 7.6, and a corresponding decrease in  $\text{H}_2\text{O}_2$  formation, with catalytic activity decreasing from 64  $\text{mol}_{\text{H}_2\text{O}_2}\text{kg}_{\text{cat}}^{-1}\text{h}^{-1}$  for the 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst only to 45  $\text{mol}_{\text{H}_2\text{O}_2}\text{kg}_{\text{cat}}^{-1}\text{h}^{-1}$  when MgO is used in addition to the catalyst. The decrease in catalytic activity is ascribed to the formation of  $\text{Mg}(\text{OH})_2$  as MgO dissolves in the reaction solution, and a resulting decrease in the stability of  $\text{H}_2\text{O}_2$ . However, it is suggested that the decrease  $\text{H}_2\text{O}_2$  yield observed is due to the greater degradation of  $\text{H}_2\text{O}_2$  as a result of the increased pH of the reaction solution rather than a decrease in catalytic activity towards the synthesis of  $\text{H}_2\text{O}_2$ .

It is possible to conclude that the use of common supports as an additive for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  can alter the pH of the reaction solution as well as catalytic activity towards  $\text{H}_2\text{O}_2$ , as a result of increasing or decreasing  $\text{H}_2\text{O}_2$  stability.

#### 3.2.5.2. Variation in pH of the water-methanol working solution using nitric and tungstic acid as an additive to 2.5 wt. % Au – 2.5 wt. % Pd / $\text{TiO}_2$ .

In order to determine if the promotive effect observed when Cs-exchanged tungstophosphoric acid is used as a solid acid additive for the direct synthesis of  $\text{H}_2\text{O}_2$  using a 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst is purely due to the change in the pH of the working solution, diluted tungstic or nitric acid were used to alter the pH of the water-methanol solvent. All other conditions remain as standard, with the acid replacing part of the water in the reaction solution. The results of this study can be seen in Figure 3.22.



**Figure 3.22.** The effect that Cs-exchanged HPAs, dilute HNO<sub>3</sub> and H<sub>2</sub>WO<sub>4</sub> has in promoting the direct synthesis of H<sub>2</sub>O<sub>2</sub>.

**Reaction conditions:** 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> (0.01g), Cs<sub>x</sub>H<sub>(3-x)</sub>PW<sub>12</sub>O<sub>40</sub> (0.05 g) or dilute HNO<sub>3</sub>, total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, , 5.6 g CH<sub>3</sub>OH + 2.9 g H<sub>2</sub>O (66 wt. % CH<sub>3</sub>OH), 2 °C.

As can be seen in Figure 3.22 the addition of both nitric acid, tungstic acid, Cs-exchanged HPAs and the parent tungstophosphoric acid, with varying mass, lowers the pH of the water methanol working solution and results in an increase in the rate of H<sub>2</sub>O<sub>2</sub> synthesis.

However the promotive effect observed when utilising either the Cs-exchanged tungstophosphoric acid or the parent, non-substituted, additive is observed to provide a greater catalytic activity when compared to the use of HNO<sub>3</sub>. Using the Cs-exchanged material or the parent acid to set pH of the working solution at approximately 2.7 is reported to produce a much more active catalyst in comparison to when HNO<sub>3</sub> is used to produce a marginally lower pH, approximately pH 2.5. As can be seen in Figure 3.22. The utilisation of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> or Cs-exchanged tungstophosphoric acid to set the pH of the working solution at approximately 2.7 results in an increase in catalytic activity from 64 mol<sub>H2O2</sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> to 299 and 305 mol<sub>H2O2</sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> for the Cs<sub>0.1</sub>H<sub>2.9</sub>PW<sub>12</sub>O<sub>40</sub> salt and parent material respectively. However the use of HNO<sub>3</sub> only improves catalytic activity to 98 mol<sub>H2O2</sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>. This is particularly interesting as it suggests that the modification of the pH of the working solution by the Cs-exchanged or parent heteropolyacid is not the sole reason for the improvement in activity towards H<sub>2</sub>O<sub>2</sub> synthesis. However further work using other, non-halide acids must be carried out to give a complete comparison of the role of conventional acids in comparison to heteropolyacids.

It is known that acidic conditions help to stabilise  $\text{H}_2\text{O}_2$ <sup>18</sup> from its subsequent degradation and that the use of acid washed supports has been found to limit or 'switch off'  $\text{H}_2\text{O}_2$  degradation.<sup>33,35</sup> It is interesting to note that when  $\text{HNO}_3$  or  $\text{H}_2\text{WO}_4$  is used to alter the pH of the reaction solution the increase in catalytic activity is much smaller than the increase seen when both the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts and tungstophosphoric acid are utilised. This trend continues even when the pH of the working solution is reduced below that possible using the heteropolyacid additives either in the Cs-exchanged form or as the parent acid. It may therefore be reasonable to assume that the reduction of solution pH may not solely cause the increase in rate of synthesis of  $\text{H}_2\text{O}_2$ . It has previously been shown in Table 3.3 that the use of  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts result in the leaching of Pd from the support, with 30 % of total Pd observed to be leached from the support when  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  is used in addition to the catalyst. It is possible that the addition of excess nitric acid results in the leaching of metals active for the direct synthesis of  $\text{H}_2\text{O}_2$  in particular Pd, in a manner similar to that observed when  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts are used in addition to 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$ .

It has previously been demonstrated (Table 3.3) that W is detected in the reaction solution regardless of Cs incorporation in the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts with a general trend reported where the amount of W detected decreases as Cs incorporation increases. This suggests that the solubility of the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salt decreases with increasing Cs content. It is shown in Figure 3.22 that activity towards  $\text{H}_2\text{O}_2$  synthesis increases with decreasing Cs content within the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salt and furthermore it has been demonstrated that this is not solely due to the decrease in reaction solution pH.

It is known that the presence of phosphate in the reaction solution is able to stabilise  $\text{H}_2\text{O}_2$ <sup>36</sup> and that the stability of the Keggin structure can be related to Cs content. As the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salt becomes less stable, with decreasing Cs content, the availability of phosphate ions ( $\text{PO}_4^{3-}$ ) in the reaction solution increases and so  $\text{H}_2\text{O}_2$  stability increases. It is therefore possible to conclude that the improvement in catalytic activity towards  $\text{H}_2\text{O}_2$  synthesis is due to a combination of decreasing reaction solution pH and an increase in the availability of  $\text{PO}_4^{3-}$ . This correlates with the trend observed in Figure 3.22, where there is an apparent increase in catalytic activity as Cs content decreases. As such it is possible to suggest that the utilisation of Cs exchanged tungstophosphoric acid as an additive for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  improves the stability of  $\text{H}_2\text{O}_2$  rather than improving catalytic activity towards the synthesis of  $\text{H}_2\text{O}_2$ .

### 3.2.7. Reusability of the Cs-exchanged HPAs in the direct synthesis of H<sub>2</sub>O<sub>2</sub>.

In order to produce a catalyst that may find industrial application it is important to ensure that the Cs-exchanged HPA additives are stable to re-use. Table 3.3 above shows that after reaction both Cs and W are detected in the reaction solution, regardless of Cs-content. The concentration of W within the solution decreases significantly as Cs loading into the Keggin structure increases. In comparison Cs content is observed to pass through a maximum of 183 ppm, when Cs loading is equal to Cs<sub>2.0</sub>. As Cs content is increased further to Cs<sub>2.5</sub> the concentration of Cs detected in the reaction solution decreases to 150 ppm. Further investigation into the reaction solution shows that Pd is present within the reaction solution when the catalyst is used in addition to the Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> salt, regardless of Cs content.

Table 3.9 shows the reusability of 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> - Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> with varying values of x. The experimental procedure is similar to that reported in Chapter 2 Section 2.3.1 for the direct synthesis of H<sub>2</sub>O<sub>2</sub>, however upon completion of the first reaction the solid is removed from the reaction solution by filtration followed by drying (110 °C, 16 h, static air). The resultant solid was then weighed to determine the extent of material lost during recovery and investigated for its activity towards the direct synthesis of H<sub>2</sub>O<sub>2</sub>.

**Table 3.9.** The reusability of 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> - Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub>.

**Reaction conditions:** Catalyst (0.01 g), Cs<sub>x</sub> H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> (0.05 g), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> =0.525, 1200 rpm, 30 min, CH<sub>3</sub>OH + 2.9 g H<sub>2</sub>O (66 Wt. % CH<sub>3</sub>OH), 2 °C.

Catalyst system	Catalyst mass post reaction / g	Productivity Fresh / mol <sub>H2O2</sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	Productivity Reuse / mol <sub>H2O2</sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>
2.5 wt. % Au – 2.5 wt. % Pd / TiO <sub>2</sub> + Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub>	0.058	188	188
2.5 wt. % Au – 2.5 wt. % Pd / TiO <sub>2</sub> + Cs <sub>2</sub> HPW <sub>12</sub> O <sub>40</sub>	0.053	239	207
2.5 wt. % Au – 2.5 wt. % Pd / TiO <sub>2</sub> + Cs <sub>0.1</sub> H <sub>2.9</sub> PW <sub>12</sub> O <sub>40</sub>	0.01	299	n.d.

Where n.d. = not able to determine

Firstly it should be noted that after reaction, filtration and recovery not all of the solid mixture of catalyst and Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> salt was recovered and for calculation of catalyst activity it was assumed that total catalyst recovery was possible. That is, any mass loss was due to the loss of Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> salt.

It is reported that the Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> salts with values of x lower than 2.5 were not stable upon re-use with the activity of the 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> - Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> physical

mixture decreasing from 239 to 207  $\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1}\text{h}^{-1}$ . This is partly explained by the incomplete recovery of the physical mixture after its first use. Secondly it was shown in Table 3.3 that there is significant loss of both Cs and W from the Keggin unit upon use of the  $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$  additive, with 183 ppm of Cs and 564 ppm of W detected in the reaction solution in addition to 2 ppm Pd. While reusability studies utilising  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  in addition to 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  were not possible due to the inability to separate  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  from the reaction solution post reaction. Although it has previously been shown (Table 3.3) that a significant amount of Pd is leached from the catalyst support when  $\text{Cs}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$  is used in addition to the 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst.

Re-use of the catalytic system utilising  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  as an acid additives shows no loss in activity towards the direct synthesis of  $\text{H}_2\text{O}_2$  and a significant increase in activity compared to the catalyst alone, with an activity of 188  $\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1}\text{h}^{-1}$  reported when  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  is used in addition to 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$ . While the catalyst alone has been shown to offer an activity of 64  $\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1}\text{h}^{-1}$ . However it has previously been shown in Table 3.3. that Pd, Cs and W are detected in the reaction solution after reaction, with a Pd concentration of 1 ppm observed. This suggests that over multiple uses catalyst activity may decrease due to the loss of Pd from the support.

It would be of great interest to investigate the stability of 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$ , when  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  is used as an additive, over longer reaction times. It may be possible to stabilise the loss of Pd and maintain the high activities reported. It is suggested that future investigation concentrates on increasing the stability of 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  in the presence of Cs-exchanged tungstophosphoric acid, as well as decreasing the solubility of  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  as this material has shown the most promise in reusability.

### 3.3. Conclusion.

Cs-exchanged heteropolyacids have been investigated as additives for 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> in the direct synthesis of H<sub>2</sub>O<sub>2</sub>. It has been shown that the addition of Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> salts where x is less than 2.5 results in the promotion of catalytic activity towards the direct synthesis of H<sub>2</sub>O<sub>2</sub> with a maximum productivity of 301 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> reported when 0.05 g of the unsubstituted H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> is utilised in addition to the 5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> catalyst. While the addition of 0.05 g of Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> causes a decrease in the rate of H<sub>2</sub>O<sub>2</sub> formation, to a minimum of 48 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>, which is ascribed to the ability of Cs to degrade H<sub>2</sub>O<sub>2</sub>. A general trend is observed where the amount of leached Cs increases as the value of x in Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> increases, to a maximum of 180 ppm for Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub>. Increasing the value of x beyond Cs<sub>2.0</sub> decreases the total amount of leached Cs to 95 ppm when the Cs<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> additive is utilised, suggesting that although Cs incorporation into the Keggin cage structure is key in reducing the solubility of tungstophosphoric acid it is not possible to completely inhibit the dissolution of the Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> salt. This is supported by the detection of W within the reaction solution, regardless of the extent of Cs exchanged.

It has been demonstrated that as the extent of Cs exchanged in to the Keggin decreases so does the pH of the reaction solution prior to the reaction occurring and it is suggested that this is partly responsible for the improvement in catalyst activity towards H<sub>2</sub>O<sub>2</sub> formation. In addition it has been reported that the use of Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> salts as additives for 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> results in the leaching of Pd from the support, with leaching of up to 30 % observed when H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> is utilised in addition to the 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> catalyst. Both of these factors are considered to be responsible for the increase in H<sub>2</sub>O<sub>2</sub> synthesis observed when Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> salts are used in addition to 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub>. Furthermore, it has been demonstrated that the presence of Cs in the reaction solution is able to degrade H<sub>2</sub>O<sub>2</sub> and a general trend is reported, where the amount of Cs detected in the reaction solution increases with increasing value of x in Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub>.

Catalyst reusability has been investigated and it is shown that retention of catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis can only be achieved when the value of x in Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> is greater than 2.5. Despite the high extent of Cs exchange required a substantial increase in activity of the catalyst towards H<sub>2</sub>O<sub>2</sub> synthesis is observed with productivity reported to increase from 64 to 188 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>. This is viewed as a meaningful step forward in the

development of the direct synthesis of  $\text{H}_2\text{O}_2$  process. However it should be noted that Cs, W and Pd are all detected within the reaction solution after use and as such it is highly likely that catalyst activity will decrease with subsequent uses.

Comparison between catalytic activity towards  $\text{H}_2\text{O}_2$  synthesis when either  $\text{HNO}_3$ ,  $\text{H}_2\text{WO}_3$  or  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts are used in addition to 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  suggests that the decrease in the reaction solution pH is not the only reason for improved  $\text{H}_2\text{O}_2$  synthesis activity. It is suggested that the presence of phosphate ions within the reaction solution, through the dissolution of the Keggin cage structure, increases  $\text{H}_2\text{O}_2$  stability and is responsible for the observed increase in catalytic activity towards  $\text{H}_2\text{O}_2$ . As Cs content within the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salt increases so does the stability of the Keggin structure and as a result the availability of  $\text{PO}_4^{3-}$  decreases.



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## 4. Ammoximation of cyclohexanone via in-situ $\text{H}_2\text{O}_2$ synthesis.

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### 4.1. Introduction.

TS-1 has been well reported as an efficient, selective catalyst for many oxidation reactions, when used alongside  $\text{H}_2\text{O}_2$ , such as alkane oxidation<sup>1</sup>, alkene epoxidation<sup>2</sup> and the formation of propylene oxide<sup>3</sup>. The ammoximation of cyclohexanone to cyclohexanone oxime is a key industrial process that utilises the excellent selectivity of TS-1 along with  $\text{H}_2\text{O}_2$ . The formation of cyclohexanone oxime is crucial in the formation of caprolactam the monomer of Nylon-6, a highly commercialised polymer that is used in a wide range of sectors, from automotive to food packaging and electrical cables.

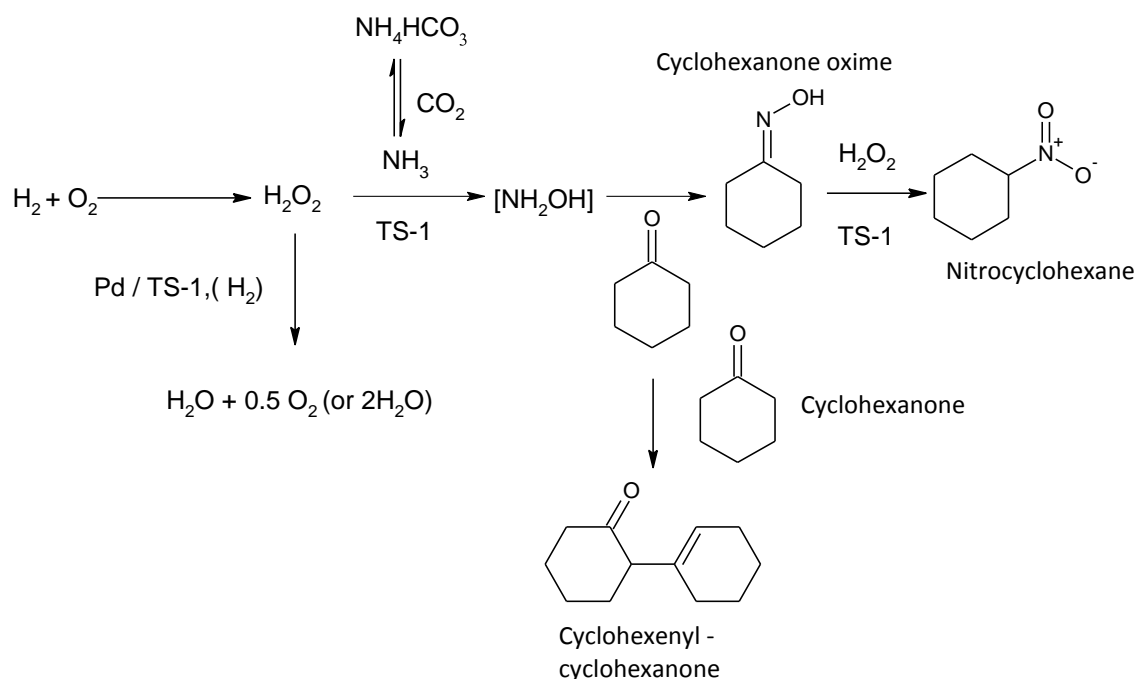
Current production of cyclohexanone oxime is reliant on the transportation and storage of large quantities of  $\text{H}_2\text{O}_2$ , with which comes inherent risk and cost. By producing  $\text{H}_2\text{O}_2$  *in-situ* it is suggested that large economic savings could be made to the industrial production of cyclohexanone oxime.

In order to investigate the feasibility of producing cyclohexanone oxime through the *in-situ* synthesis of  $\text{H}_2\text{O}_2$  catalysts utilising commercial TS-1 as a support have been prepared by impregnation. Their activity towards the direct synthesis of  $\text{H}_2\text{O}_2$ , at sub-ambient and elevated temperatures using conditions established from literature<sup>4-6</sup>, have been investigated and following on from this the activity of a model 5 % Pd / TS-1 catalyst towards  $\text{H}_2\text{O}_2$  synthesis and subsequent degradation under conditions similar to those used for the ammoximation reaction, via the addition of  $\text{H}_2\text{O}_2$ , was also examined.

Following this mono- and bi-metallic Au-Pd catalysts supported on TS-1 were evaluated for their activity towards the ammoximation of cyclohexanone to cyclohexanone oxime via addition of pre-formed  $\text{H}_2\text{O}_2$ , in a manner to that already reported within the literature<sup>7</sup>. Finally using a model 5 wt. % Pd / TS-1 reaction conditions were established for the ammoximation of cyclohexanone via the *in-situ* synthesis of  $\text{H}_2\text{O}_2$  from  $\text{H}_2$  and  $\text{O}_2$ .

Figure 4.1 is a proposed reaction scheme for the ammoximation of cyclohexanone to cyclohexanone oxime via the *in-situ* generation of  $\text{H}_2\text{O}_2$ . It is known that many catalysts that are active towards the direct synthesis of  $\text{H}_2\text{O}_2$  are also active towards the degradation of

H<sub>2</sub>O<sub>2</sub>. However it is suggested that due to the use of elevated temperatures and presence of basic conditions, in the form of NH<sub>3</sub>, the development of a catalyst that is inactive towards H<sub>2</sub>O<sub>2</sub> degradation would have minimal impact on limiting overall breakdown of H<sub>2</sub>O<sub>2</sub>. Furthermore it has been reported that a number of minor organic by-products may be formed, either through the reaction of cyclohexanone oxime with H<sub>2</sub>O<sub>2</sub> to form nitrocyclohexane or the homogeneous reaction of cyclohexanone to yield cyclohexenylcyclohexanone and cyclohexanone azine <sup>8</sup>.



**Figure 4.1.** Proposed reaction scheme for the ammoxidation of cyclohexanone via *in-situ* generation of H<sub>2</sub>O<sub>2</sub>.

## 4.2. Results.

Supported Au / Pd as well as bi-metallic catalysts were prepared on TS-1 by the standard impregnation methods as outlined in Chapter 2 using PdCl<sub>2</sub> and HAuCl<sub>4</sub>. All H<sub>2</sub>O<sub>2</sub> synthesis and degradation testing as well as cyclohexanone oxime synthesis, via *in-situ* formation of H<sub>2</sub>O<sub>2</sub> or the addition of pre-formed H<sub>2</sub>O<sub>2</sub> were carried out according to the procedures outlined in Chapter 2.

A summary of the standard testing conditions is outlined below:

1. H<sub>2</sub>O<sub>2</sub> direct synthesis reaction conditions: Catalyst (0.01 g), MeOH (5.6 g), H<sub>2</sub>O (2.9 g), 5 % H<sub>2</sub> / CO<sub>2</sub> (2.9 MPa) and 25 % O<sub>2</sub> / CO<sub>2</sub> (1.1 MPa), 30min, 2 °C, 1200 rpm.

2. H<sub>2</sub>O<sub>2</sub> degradation reaction conditions: Catalyst (0.01 g), MeOH (5.6 g), H<sub>2</sub>O (2.22g), H<sub>2</sub>O<sub>2</sub> (0.68 g 50 wt. %) 5 % H<sub>2</sub>/CO<sub>2</sub> (2.9 MPa) 30min, 2 °C, 1200 rpm.
3. Ammoximation of cyclohexanone via the addition of pre-formed H<sub>2</sub>O<sub>2</sub> reaction conditions: Catalyst (0.05 g), cyclohexanone (10 mmol), NH<sub>3</sub> (28 wt. % 12 mmol), H<sub>2</sub>O (2.5 g), t-BuOH (2.5 g), 80 °C, 35 wt. % H<sub>2</sub>O<sub>2</sub> (10 mmol, 0.89 mlhr<sup>-1</sup> then 0.5 h stir).
4. Cyclohexanone ammoximation reaction conditions: Catalyst (0.05 g), t-BuOH (5.6 g), H<sub>2</sub>O (2.69 g), cyclohexanone (0.13 g), NH<sub>3</sub> (28 Wt. %, 0.079 g), 5 % H<sub>2</sub>/ CO<sub>2</sub> (2.9 MPa) and 25 % O<sub>2</sub>/CO<sub>2</sub> (1.1 MPa), 30 min, 80 °C, 1200 rpm.

#### 4.2.1. H<sub>2</sub>O<sub>2</sub> synthesis activity of monometallic and bimetallic Au-Pd catalysts supported on TS-1.

Monometallic catalysts were prepared by impregnation containing 5 wt. % Au or 5 wt. % Pd using TS-1 as a support material. These catalysts were calcined at 400 °C for 3h in static air. Bi-metallic catalysts were prepared containing 5 wt. % Pd - Au on TS-1 in a 1 : 1 ratio and calcined in a similar manner.

Initial studies were conducted to determine the ability of Au, Pd and Au-Pd catalysts to synthesise H<sub>2</sub>O<sub>2</sub>, using standard reaction conditions, outlined in Chapter 2, Section 2.3.1. Further work was then conducted at higher temperatures (30 °C). Table 4.1 compares H<sub>2</sub>O<sub>2</sub> synthesis rates at 2 and 30 °C using a water (H<sub>2</sub>O) / methanol (MeOH) solvent system.

**Table 4.1** Catalytic activity towards the direct synthesis of H<sub>2</sub>O<sub>2</sub>, in a H<sub>2</sub>O / MeOH solvent system.

Catalyst	H <sub>2</sub> O <sub>2</sub> productivity / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> (2 °C)	H <sub>2</sub> O <sub>2</sub> productivity/ mol <sub>H<sub>2</sub>O<sub>2</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> (30 °C)
5 wt. % Au / TS-1	2	0
2.5 wt. % Au- 2.5 wt. % Pd / TS-1	100	19
5 wt. % Pd / TS-1	116	26
2.5 wt. % Au- 2.5 wt. % Pd / Al <sub>2</sub> O <sub>3</sub>	15 <sup>9</sup>	0
2.5 wt. % Au- 2.5 wt. % Pd / TiO <sub>2</sub>	64 <sup>10</sup>	36
2.5 wt. % Au- 2.5 wt. % Pd / SiO <sub>2</sub>	108 <sup>11</sup>	51
2.5 wt. % Au- 2.5 wt. % Pd / C	110 <sup>12</sup>	55

**Reaction conditions:** Catalyst (0.01 g), 580 psi, H<sub>2</sub> / O<sub>2</sub> =0.525, 1200 rpm, 30 min, 5.6 g MeOH + 2.9 g H<sub>2</sub>O (66 wt. % CH<sub>3</sub>OH), X °C.

Catalysts calcined 3 h, 400 °C, static air, 20 °C min<sup>-1</sup>

It is observed that the TS-1 supported Au, Pd, Au-Pd, catalysts are active towards the direct synthesis of H<sub>2</sub>O<sub>2</sub> and at sub-ambient temperatures the bi-metallic Au-Pd catalysts are observed to have greater rates of H<sub>2</sub>O<sub>2</sub> synthesis than analogous catalysts supported on TiO<sub>2</sub> (64 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>)<sup>13</sup> and Al<sub>2</sub>O<sub>3</sub> (15 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>)<sup>9</sup> and have comparable activity to the corresponding SiO<sub>2</sub> (108 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>)<sup>14</sup> and carbon supported catalyst (110 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>)<sup>11</sup>.

As expected when higher temperatures are investigated the rate H<sub>2</sub>O<sub>2</sub> synthesis decreases for all catalysts investigated. Both the 5 wt. % Pd and 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 catalysts are observed to lose approximately 80 % of their activity toward H<sub>2</sub>O<sub>2</sub> synthesis, with productivity values of 26 and 19 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> reported for the 5 wt. % Pd and 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 catalysts respectively. This is ascribed to an increase in the rate of H<sub>2</sub>O<sub>2</sub> degradation, it is known that H<sub>2</sub>O<sub>2</sub> stability decreases as temperature increases. It has previously been reported by Hutchings and co-workers<sup>15</sup> that raising reaction temperature results in an increase in the conversion of H<sub>2</sub>, from 20 % at 2 °C to 30 % at 30 °C, but a corresponding decrease in selectivity towards H<sub>2</sub>O<sub>2</sub>. It has been reported by Freakley *et.al.*<sup>15</sup> that as reaction temperature is increased the solubility of O<sub>2</sub> in both water and methanol decreases, resulting in a decrease in the rate of H<sub>2</sub>O<sub>2</sub> synthesis. In addition

Freakley *et.al.*<sup>15</sup> report that an increase in temperature results in an increase in H<sub>2</sub> solubility in methanol, as such the rate of hydrogenation of H<sub>2</sub>O<sub>2</sub> is expected to be greater at elevated temperatures and these two factors combined result in a decrease in H<sub>2</sub>O<sub>2</sub> selectivity.

Interestingly, the activity of the 5 wt. % Pd / TS-1 catalyst is observed to be greater than that of the 2.5 wt. % Au- 2.5 wt. % Pd / TS-1 when investigated at both 2 and 30 °C. This is somewhat at odds with previous work conducted by Hutchings and co-workers, who have shown that, on a range of supports the incorporation of Au onto a Pd-only catalyst improves catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis beyond that of the monometallic catalysts<sup>13 9 16</sup>. This has been ascribed to the formation of core-shell metal nanoparticles and the electronic modification of Pd by Au<sup>17</sup>. It would be of great interest to investigate particle morphology and the extent of alloying of Au and Pd on a TS-1 support to determine if a similar particle morphology is adopted when utilising this support. It has previously been demonstrated that when utilising a carbon support<sup>17</sup> Au-Pd nanoparticles adopt a random alloy, unlike when oxide supports such as TiO<sub>2</sub> are used<sup>17</sup>. It may be that in a similar manner to when carbon is used as a support the metal nanoparticles adopt a random alloy morphology, rather than a Au-core PdO-shell morphology.

#### 4.2.2. The direct synthesis of H<sub>2</sub>O<sub>2</sub>, using 5 wt. % Pd/ TS-1 as a model catalyst, moving towards ammoximation conditions.

The direct synthesis of H<sub>2</sub>O<sub>2</sub> has been well studied by Hutchings *et.al.*<sup>4, 13</sup> using a H<sub>2</sub>O - MeOH solvent system, due to the high solubility of H<sub>2</sub> in MeOH and conversely the high solubility of O<sub>2</sub> in H<sub>2</sub>O. Wu *et.al.*<sup>18</sup> has shown that when tertiary / t- butanol (t-BuOH) is used as a solvent superior levels of both cyclohexanone conversion and oxime selectivity are observed when compared to H<sub>2</sub>O, toluene and MeOH when TS-1 is used as the catalyst for the ammoximation of cyclohexanone. Further investigation by Francesconi and co-workers<sup>19</sup> have shown that the solubility of hydrogen increases with alcohol chain length. Therefore, in order to find a balance between high solubility of H<sub>2</sub> and O<sub>2</sub> and superior selectivity towards cyclohexanone oxime a mixed H<sub>2</sub>O / t-BuOH solvent system was chosen to investigate the ammoximation reaction via *in-situ* H<sub>2</sub>O<sub>2</sub> generation and firstly for the direct synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub>. Further investigation on the role of solvent composition is carried out below in Section 4.3.4.

Table 4.2 compares the H<sub>2</sub>O<sub>2</sub> synthesis rates of 5 wt. % Pd / TS-1 in a H<sub>2</sub>O / t-BuOH solvent system under various temperatures (30 - 80 °C) and in the presence of cyclohexanone and NH<sub>3</sub>.

**Table 4.2.** Direct synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> in H<sub>2</sub>O/t-BuOH solvent system.

Temperature / °C	Solvent only		Cyclohexanone present <sup>(a)</sup>		NH <sub>3</sub> present <sup>(b)</sup>	
	H <sub>2</sub> O <sub>2</sub> productivity / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	H <sub>2</sub> Conversion / %	H <sub>2</sub> O <sub>2</sub> productivity / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	H <sub>2</sub> Conversion / %	H <sub>2</sub> O <sub>2</sub> productivity / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	H <sub>2</sub> Conversion / %
30	60	10	55	9	0	10
50	12	13	10	12	0	12
80	7	17	5	15	0	16

**Reaction conditions:** 5 wt. %Pd / TS-1 (0.01 g), 580 psi, H<sub>2</sub> / O<sub>2</sub> =0.525, 1200 rpm, 30 min, 5.6 g t-BuOH + 2.9 g H<sub>2</sub>O (66 Wt. % t-BuOH), X °C. <sup>(a)</sup> cyclohexanone (0.13 g 1.3 mmol), <sup>(b)</sup> NH<sub>3</sub> (28 wt. %, 0.08 g 1.3 mmol).

It has been shown that the solubility of H<sub>2</sub> in alcohols increases with chain length<sup>19</sup>, and as such it is likely that the rate of H<sub>2</sub>O<sub>2</sub> synthesis is linked to the number of carbon atoms present in the solvent chain. This is demonstrated when the rate of H<sub>2</sub>O<sub>2</sub> synthesis using a H<sub>2</sub>O / MeOH and H<sub>2</sub>O / t-BuOH solvent system are compared. H<sub>2</sub>O<sub>2</sub> productivity for the 5 wt. % Pd / TS-1 catalyst increases from 26 to 60 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> with increasing alcohol chain length, at 30 °C.

As can be seen in Table 4.2 the catalytic activity towards H<sub>2</sub>O<sub>2</sub> decreases from 60 to 7 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> as temperature increases to 80 °C. This is as expected, as H<sub>2</sub>O<sub>2</sub> productivity is determined at the end of the reaction and is therefore not a measure of total H<sub>2</sub>O<sub>2</sub> synthesis but of how much is remaining post reaction. It is known that H<sub>2</sub>O<sub>2</sub> is unstable at elevated temperatures<sup>20</sup> and as such it is expected that lower rates of H<sub>2</sub>O<sub>2</sub> synthesis would be observed.

When cyclohexanone is incorporated into the system there is a small decrease in the synthesis rate of H<sub>2</sub>O<sub>2</sub>, from 60 to 55 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. This may be due to partial inhibition of active sites responsible for H<sub>2</sub>O<sub>2</sub> synthesis, a decrease in H<sub>2</sub> solubility when cyclohexanone is present or the use of H<sub>2</sub> in the reduction of cyclohexanone resulting in less H<sub>2</sub> available for H<sub>2</sub>O<sub>2</sub> synthesis.

The presence of NH<sub>3</sub> results in no H<sub>2</sub>O<sub>2</sub> being detected at the end of the reaction. Again this is unsurprising as it is known that H<sub>2</sub>O<sub>2</sub> is unstable in the presence of basic conditions<sup>21</sup>. It is possible that under the conditions utilised some NH<sub>3</sub> utilised in the formation of NH<sub>2</sub>OH and it is suggested that the extent of hydroxylamine formation could be quantified via the addition of cyclohexanone and measurement of the resultant yield of cyclohexanone oxime.



#### 4.2.3. The degradation of H<sub>2</sub>O<sub>2</sub> using 5 wt. % Pd / TS-1 as a model catalyst, moving towards ammoximation conditions.

For a catalytic system to be efficient towards H<sub>2</sub>O<sub>2</sub> synthesis the rate of catalytic breakdown of H<sub>2</sub>O<sub>2</sub> must be limited as much as possible. Furthermore the ability of the solvent, cyclohexanone and NH<sub>3</sub> to contribute to H<sub>2</sub>O<sub>2</sub> degradation must also be understood. The conditions utilised for the ammoximation of cyclohexanone via *in-situ* synthesis of H<sub>2</sub>O<sub>2</sub> are quite challenging as H<sub>2</sub>O<sub>2</sub> readily decomposes at elevated temperatures and in basic conditions, it is therefore important to determine how effective these reaction conditions are at decomposing H<sub>2</sub>O<sub>2</sub>. Table 4.3 outlines the effect of the reaction conditions towards the degradation of 12 wt. % H<sub>2</sub>O<sub>2</sub> in a t-BuOH / H<sub>2</sub>O solvent mixture in the presence of cyclohexanone and / or NH<sub>3</sub> and a 5 wt. % Pd / TS-1 catalyst. Standard H<sub>2</sub>O<sub>2</sub> degradation testing, as outlined in Chapter 2, Section 2.3.2, utilises a lower concentration of H<sub>2</sub>O<sub>2</sub> (4 wt. %). However as the reaction conditions are known to be unfavourable towards H<sub>2</sub>O<sub>2</sub> stability it was decided to use a greater concentration of H<sub>2</sub>O<sub>2</sub> (12. wt. %).

**Table 4.3.** Comparison of H<sub>2</sub>O<sub>2</sub> degradation at 30 °C in the presence and absence of 5 Wt. % Pd / TS-1.

	H <sub>2</sub> O <sub>2</sub> degradation /	
	%	
	No catalyst	Catalyst
Solvent system only	0	35
Solvent + Cyclohexanone	14	38
Solvent + NH <sub>3</sub>	71	82
Solvent + Cyclohexanone + NH <sub>3</sub>	76	85

**Reaction conditions:** 5 wt. % Pd / TS-1 (0.01 g), 580 psi, H<sub>2</sub> / O<sub>2</sub> =0.525, 1200 rpm, 30 min, 5.6 g t-BuOH + 0.86 g H<sub>2</sub>O, 2.04 g H<sub>2</sub>O<sub>2</sub> (50 Wt. %), 28 wt. % NH<sub>3</sub> (0.08 g 1.3 mmol), cyclohexanone (0.13 g 1.3mmol), 30 °C.

It is observed that the solvent system does not contribute to the degradation of H<sub>2</sub>O<sub>2</sub> in the absence of catalyst, cyclohexanone or ammonia. This is particularly interesting as it is expected that some degradation of H<sub>2</sub>O<sub>2</sub> would be observed at an elevated temperature. Upon introduction of the 5 wt. % Pd / TS-1 catalyst a dramatic increase in H<sub>2</sub>O<sub>2</sub> degradation is observed, with 35 % degradation reported.

The introduction of cyclohexanone leads to a slight increase in the rate of H<sub>2</sub>O<sub>2</sub> degradation. With degradation reported to be 14 % in the absence of catalyst and 38 % when the catalyst

is present and this correlates with the slight decrease in the rate of  $\text{H}_2\text{O}_2$  synthesis observed when cyclohexanone is present, shown in Table 4.2.

Unsurprisingly the introduction of  $\text{NH}_3$  to the solvent system leads to a rise in the breakdown of  $\text{H}_2\text{O}_2$ , to 71 % in the absence of the catalyst respectively. This is expected due to the low stability of  $\text{H}_2\text{O}_2$  under basic conditions. Upon addition of the catalyst a rise in  $\text{H}_2\text{O}_2$  degradation is observed, to 82 %. It is suggested that the relatively small increase in  $\text{H}_2\text{O}_2$  degradation with catalyst addition is due to limitations in mass transfer of the  $\text{H}_2\text{O}_2$  to the catalyst, the  $\text{NH}_3$  present in solution readily decomposes  $\text{H}_2\text{O}_2$  before it can reach catalytic sites responsible for its degradation. Combination of both cyclohexanone and  $\text{NH}_3$  results in a further increase in  $\text{H}_2\text{O}_2$  degradation, to 76 % when no catalyst is present and 85 % when a catalyst is introduced.

The data shown in Table 4.3 demonstrates the ability of the reaction conditions to contribute to  $\text{H}_2\text{O}_2$  degradation and highlights the difficulties associated with the in-situ synthesis of  $\text{H}_2\text{O}_2$  in the ammoximation reaction. However it is suggested that by improving catalyst selectivity towards  $\text{H}_2\text{O}_2$  it is possible to more efficiently utilise the reactants, in particular  $\text{H}_2$ , and reduce costs to any future industrial application.

#### 4.2.4. The ammoximation of cyclohexanone to cyclohexanone oxime via $\text{H}_2\text{O}_2$ addition.

The monometallic and bimetallic Au-Pd catalysts prepared by impregnation were tested for the ammoximation of cyclohexanone via the addition of pre-formed  $\text{H}_2\text{O}_2$ . These catalysts were compared to the bare TS-1 material, following the procedure is outlined in Chapter 2. But is shown below for clarity:

Cyclohexanone (1.0 g, 10 mmol), catalyst (0.05 g), t-BuOH (2.5 g),  $\text{H}_2\text{O}$  (2.5 g) and 28 wt. %  $\text{NH}_3$  (12 mmol, 0.73 g) were added into a two neck flask with condenser attached. The second flask neck is equipped with a  $\text{H}_2\text{O}_2$  inlet line. The reaction mixture was heated, with stirring, to 80 °C and  $\text{H}_2\text{O}_2$  (35 wt. %, 10 mmol, 0.89 g) was added over 1 h using a HPLC pump, at a rate of 0.0148 mlmin<sup>-1</sup>. The reaction was allowed to continue for a further 0.5 h. After this time the reaction mixture was allowed to cool to room temperature and ethanol (10 ml) and internal standard (diethylene glycol monoethyl ether) (1.0 g) are added. The catalyst is removed by filtration and the mixture is analysed by gas chromatography.

The ability of the catalyst to convert cyclohexanone and catalyst selectivity towards the oxime was determined by gas chromatography. Catalytic re-use was also investigated in a manner similar to that outlined above. The results are summarised in Table 4.4.

**Table 4.4.** Comparison of fresh Au, Pd, and Au-Pd loaded TS-1 and non-metal loaded TS-1 for the ammoximation of cyclohexanone via the addition of H<sub>2</sub>O<sub>2</sub>.

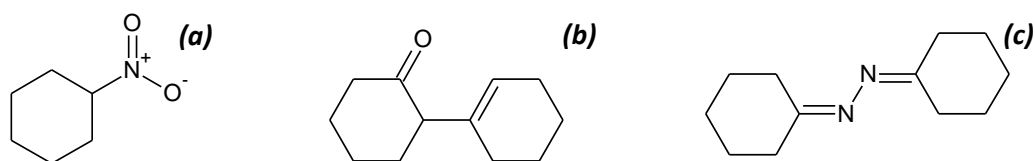
Unused Catalyst		
Catalyst	Cyclohexanone Conversion / %	Oxime Selectivity / %
TS-1	40	70
5 wt. % Au / TS-1	39	72
2.5 wt. % Au- 2.5 wt. % Pd / TS-1	34	67
5 wt. % Pd / TS-1	36	64
Used Catalyst		
TS-1	40	30
5 wt. % Au / TS-1	39	14
2.5 wt. % Au- 2.5 wt. % Pd / TS-1	33	24
5 wt. % Pd / TS-1	33	18

**Reaction Conditions:** Catalyst (0.05 g), cyclohexanone (10 mmol), NH<sub>3</sub> (28 wt. % 12 mmol), H<sub>2</sub>O (2.5 g), t-BuOH (2.5 g), 80 °C, 35 wt. % H<sub>2</sub>O<sub>2</sub> (10 mmol, 0.89 mlhr<sup>-1</sup> then 0.5 h stir).

It is reported that the monometallic and bimetallic Au-Pd catalysts show similar levels of cyclohexanone conversion and selectivity towards cyclohexanone oxime as the bare TS-1. The non-metal containing TS-1 material is reported to offer 70 % selectivity towards the oxime, and conversion rates of 40 %, while both of these measures vary slightly when Au and Pd are incorporated onto the support. This suggests that the introduction of these metals do not adversely effect the activity of the support towards the ammoximation of cyclohexanone to a great extent and that the presence of the metal on the support does not block availability to the Ti(IV) sites, believed to be key in the formation of hydroxylamine. These catalysts may show promise for the ammoximation of cyclohexanone via *in-situ* H<sub>2</sub>O<sub>2</sub> synthesis.

Catalytic reusability was investigated, where the material were dried at 110 °C for 16 h prior to re-use. Upon re-use a similar extent of conversion of cyclohexanone to the fresh materials was observed, whereas a dramatic decrease in selectivity towards cyclohexanone oxime was determined. The use of basic reaction conditions are known to lead to the loss of Ti from the framework of TS-1 resulting in the deactivation of TS-1<sup>22</sup>. It is believed that this may partially explain the loss in selectivity towards cyclohexanone oxime. Furthermore, it is known that the formation of organic by-products such as; nitrocyclohexane, cyclohexenylcyclohexanone and cyclohexanone azine, seen in Figure 4.2, can all contribute to catalyst deactivation via

blocking of the pore system within TS-1, preventing access to Ti(IV) sites<sup>18</sup> required to activate H<sub>2</sub>O<sub>2</sub>. It may be that the formation of these un-wanted by-products become more dominant upon catalyst re-use and a further investigation into the products formed upon catalyst re-use would be beneficial. As would investigation into catalyst regeneration. However as this study is primarily an investigation into the ability of precious metals supported on TS-1 to catalyse the ammoximation of cyclohexanone via *in-situ* H<sub>2</sub>O<sub>2</sub> synthesis, that is in the presence of a reducing atmosphere and dilute carbonic acid present in the reaction solution due to the use of CO<sub>2</sub> as a diluent for the reactant gasses (H<sub>2</sub> and O<sub>2</sub>) it was not thought prudent to heavily characterise the catalysts described in this section of work. It is possible to conclude that the incorporation of Au and Pd onto TS-1 does not adversely affect the ability of the support to catalyse the formation of cyclohexanone oxime. Furthermore the work of Wu *et.al.* has demonstrated that the use of high temperatures, 80 °C, is able to negate the formation of unwanted by-products during the ammoximation of cyclohexanone<sup>18</sup>, via the addition of pre-formed H<sub>2</sub>O<sub>2</sub>. As such it is the extent of pore blocking by by-products may be minimal.



**Figure 4.2.** Unwanted by-products reported during the ammoximation of cyclohexanone to cyclohexanone oxime. *(a)* Nitrocyclohexane, *(b)* Cyclohexenylcyclohexanone, *(c)* Cyclohexanone azine.

#### 4.3. Optimisation of Reaction Conditions for the Ammoximation of Cyclohexanone to Cyclohexanone Oxime.

Previously it has been shown that Au / Pd / Au – Pd / TS-1 catalysts are active for both the direct synthesis of H<sub>2</sub>O<sub>2</sub> and the ammoximation of cyclohexanone through the addition of H<sub>2</sub>O<sub>2</sub> (Sections 4.2.1 and 4.2.4).

The ability of these materials to catalyse the ammoximation of cyclohexanone via *in-situ* H<sub>2</sub>O<sub>2</sub> synthesis is evaluated below using 5 wt. % Pd / TS-1 as a model catalyst. Further investigation in to the role of catalyst design in improving this approach to the ammoximation of cyclohexanone is outlined in the following Chapter.

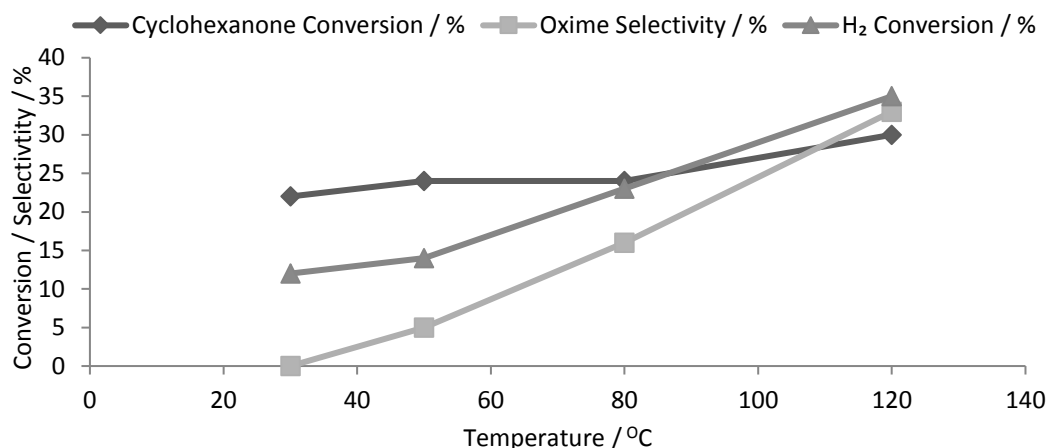
As discussed above the reaction conditions utilised in the ammoximation of cyclohexanone are not conducive H<sub>2</sub>O<sub>2</sub> stability, in particular the use elevated temperatures and presence

of base can lead to high rates of  $\text{H}_2\text{O}_2$  degradation. Furthermore it has been shown that the ratio of reactants ( $\text{H}_2\text{O}_2$  :  $\text{NH}_3$  : cyclohexanone) is key in producing a highly selective process for the ammoximation reaction utilising addition of  $\text{H}_2\text{O}_2$ <sup>23, 24</sup>. It is therefore important to use reaction conditions that find a balance between optimal cyclohexanone conversion and selectivity towards cyclohexanone oxime as well as  $\text{H}_2\text{O}_2$  synthesis and overall stability of the catalyst. To this end the reaction conditions utilised in the ammoximation of cyclohexanone to cyclohexanone oxime via *in-situ*  $\text{H}_2\text{O}_2$  synthesis were investigated. For any process to be industrially feasible catalyst stability is very important, to this end the leaching of Pd from the support was measured as a function of solvent composition as well as cyclohexanone and  $\text{NH}_3$  concentration.

#### 4.3.1. Reaction temperature optimisation.

The optimal temperature for the industrial ammoximation process has been reported to be between 80-90 °C, with excess temperatures suggested to limit the availability of both  $\text{H}_2\text{O}_2$  and  $\text{NH}_3$ , due to degradation or vaporisation<sup>25</sup>. While  $\text{H}_2\text{O}_2$  direct synthesis has been shown to favour sub-ambient temperatures<sup>13, 20</sup>, as  $\text{H}_2\text{O}_2$  rapidly decomposes to  $\text{H}_2\text{O}$  at elevated temperatures. Finding a balance between these two processes offers a major initial challenge, rapid  $\text{H}_2\text{O}_2$  decomposition may limit the synthesis of  $\text{NH}_2\text{OH}$  as  $\text{H}_2\text{O}_2$  is unable to reach the Ti (IV) sites present on the TS-1. The formation of this intermediate is believed to be key in the ammoximation of cyclohexanone<sup>26</sup>.

As has been shown in Section 4.2.2 above it is possible to make  $\text{H}_2\text{O}_2$  in a  $\text{H}_2\text{O}$  / t-BuOH solvent at elevated temperatures. It is highly likely that at temperatures as high as 80 °C  $\text{H}_2\text{O}_2$  can be synthesised, however  $\text{H}_2\text{O}_2$  'lifetime' may be very short due to the high decomposition rate at such a high temperature and as  $\text{H}_2\text{O}_2$  concentration is determined at the end of the reaction it is not possible to determine true values for catalytic activity towards  $\text{H}_2\text{O}_2$  synthesis. Figure 4.3 shows the effect of reaction temperature on the ammoximation of cyclohexanone via *in-situ*  $\text{H}_2\text{O}_2$  synthesis.



**Figure 4.3.** The effect of reaction temperature on the ammoximation of cyclohexanone.

**Reaction conditions:** 5 wt. % Pd / TS-1 (0.05 g), cyclohexanone (0.13 g, 1.3mmol), NH<sub>3</sub> (0.08 g, 28 wt %, 1.3 mmol), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> =0.525, 1200 rpm, 90 min, 5.6 g t-BuOH + 2.69 g H<sub>2</sub>O (66 wt. % t-BuOH), X °C.

It can be seen that for any significant oxime synthesis to be observed a temperature of 80 °C (where selectivity and cyclohexanone conversion are reported as 16 and 24 % respectively) is required. This is found to correlate well with temperatures reported in literature for the ammoximation process via the addition of H<sub>2</sub>O<sub>2</sub><sup>18</sup> below this temperature it is found that the formation of un-wanted organic by-products can dominate<sup>27</sup>. Further increasing temperature to 120 °C causes a rise in conversion to 33 %, while selectivity increases to 30 %. It has been suggested by Dal Pozzo and co-workers<sup>26</sup> that at higher temperatures the formation unwanted inorganic by-products, in particular nitrites and nitrates, occurs less readily as the competitive catalytic formation of hydroxylamine is kinetically predominant to the oxidation of ammonia by H<sub>2</sub>O<sub>2</sub>.

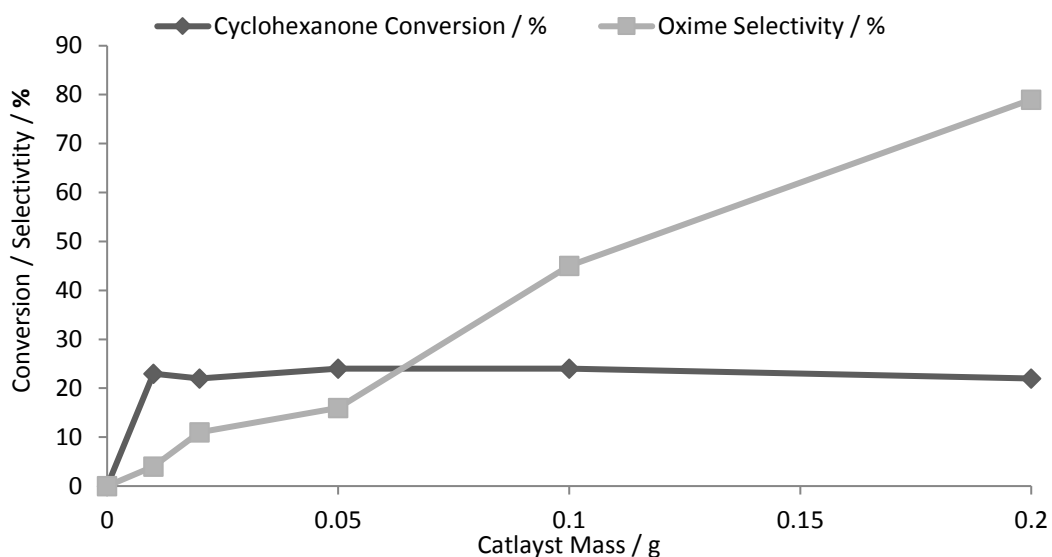
It can be observed that as reaction temperature increases so does the extent of H<sub>2</sub> conversion, increasing from 12 to 35 % as the reaction temperature increases from 30 to 120 °C. It has been reported by Freakley *et.al.*<sup>15</sup> that increasing reaction temperature in a water – methanol solvent system leads to a decrease in the solubility of oxygen in both water and methanol, while the solubility of H<sub>2</sub> increases in methanol. This results in an increase in the rate of hydrogenation of H<sub>2</sub>O<sub>2</sub> and a decrease in the rate of H<sub>2</sub>O<sub>2</sub> synthesis. It is suggested that a similar effect is observed in Figure 4.2. That is at increased temperatures the solubility of H<sub>2</sub> is greater in the solvent and with more H<sub>2</sub> present in the system the rate of H<sub>2</sub>O<sub>2</sub> hydrogenation is increased. However as O<sub>2</sub> solubility decreases the rate of H<sub>2</sub>O<sub>2</sub> formation decreases, by decreasing the rate of H<sub>2</sub>O<sub>2</sub> formation it is possible to ensure that the available Ti(IV) sites of the TS-1 support are able to readily activate H<sub>2</sub>O<sub>2</sub> to allow for hydroxylamine formation.

Furthermore, the formation of ammonia salts, such as ammonium carbonate at ambient temperatures, when the autoclave is charged with reactant gases ( $\text{O}_2 / \text{CO}_2$  and  $\text{H}_2 / \text{CO}_2$ ) will result in a decrease in the rate of hydroxylamine formation. As temperature increases so does the rate of ammonium carbonate decomposition, and it may be that this causes the ratio of reactants to be closer to 1 : 1 : 1 and as such as improvement in selectivity is observed.

Finally increased temperature may result in improvement in reactant diffusion, this means that there is increased diffusion of  $\text{NH}_3$  to Ti (IV) sites present on the support as well as diffusion of hydroxylamine from the support to cyclohexanone and as such conversion of cyclohexanone is improved. However as the reaction solution is stirred at 1200 rpm the effect of increased temperature on diffusion is believed to be minimal at best.

#### 4.3.2. Catalyst mass optimisation.

Figure 4.4 shows the effect of catalyst mass on the ammoximation of cyclohexanone to cyclohexanone oxime.



**Figure 4.4.** The effect of catalyst mass on the ammoximation of cyclohexanone.

**Reaction conditions:** 5 wt. % Pd / TS-1 (X g), cyclohexanone (0.13 g, 1.3 mmol),  $\text{NH}_3$  (0.08 g, 28 wt. %, 1.3 mmol), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 90 min, 5.6 g t-BuOH + 2.69 g  $\text{H}_2\text{O}$  (66 wt. % t-BuOH), 80 °C.

Firstly it should be noted that in the absence of catalyst there is no conversion of cyclohexanone and no oxime is detected. Furthermore it can be seen that increasing catalyst mass leads to improvement in catalytic selectivity but not conversion, by increasing catalyst mass from 0.01g to 0.2 g selectivity increases by almost 20 times from 4 to 79 %. It is

reasonable to expect that by using more catalyst there is greater availability of Ti (IV) sites and so conversion of  $\text{H}_2\text{O}_2$  to hydroxylamine is likely to increase.

The utilisation of more 5 Wt. % Pd / TS-1 is likely to lead to an increase in the concentration of  $\text{H}_2\text{O}_2$ , however it is known that many catalysts active for the direct synthesis of  $\text{H}_2\text{O}_2$  are also active for its subsequent degradation and as such it is unclear if the net  $\text{H}_2\text{O}_2$  synthesis is increased with increasing catalyst amount. In this case it is possible that the net synthesis of  $\text{H}_2\text{O}_2$  changes very little as the increase in synthesis rate is offset by increasing catalytic degradation of  $\text{H}_2\text{O}_2$ . However, it may also be possible that the formation of  $\text{H}_2\text{O}_2$  is limited by diffusion of  $\text{H}_2$  and  $\text{O}_2$  to the active sites present on the catalyst. But the increased availability of Ti(IV) sites means that once  $\text{H}_2\text{O}_2$  is formed it is utilised more selectively in the formation of hydroxylamine and not degraded to water by the reaction conditions or catalyst.

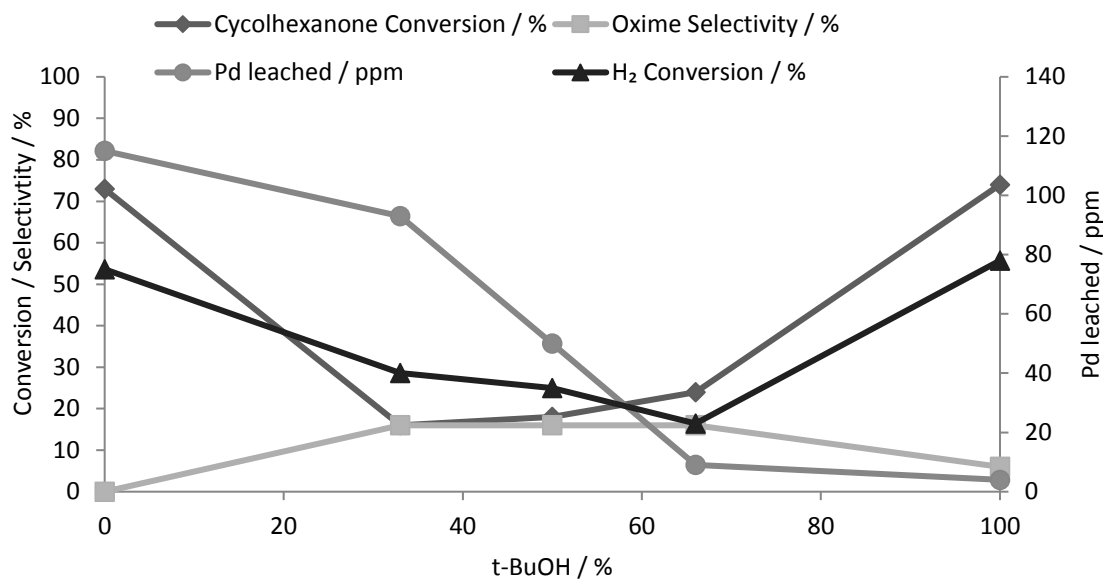
The presence of more Ti(IV) sites may mean that the conversion of  $\text{H}_2\text{O}_2$  and  $\text{NH}_3$  to  $\text{NH}_2\text{OH}$  is increased, that is selectivity towards hydroxylamine based on  $\text{H}_2\text{O}_2$  increases, and so the selectivity towards the oxime is increased as catalyst mass utilised rises. In comparison to selectivity conversion remains fairly static regardless of total catalyst loading.

#### 4.3.3. Solvent composition optimisation

It has been reported that the presence of t-butanol (t-BuOH) improves both catalytic stability, conversion of cyclohexanone and selectivity towards the oxime for the ammoximation process with the addition of pre-formed  $\text{H}_2\text{O}_2$ <sup>18</sup>. While the direct synthesis of  $\text{H}_2\text{O}_2$  has been highly studied using a  $\text{H}_2\text{O}$ / MeOH mixture as this offers high solubility of both  $\text{H}_2$  and  $\text{O}_2$  and furthermore aids in stabilising  $\text{H}_2\text{O}_2$ . However from an environmental and economic perspective the use of  $\text{H}_2\text{O}$  as a solvent may be beneficial.

Figure 4.5 shows the effect of solvent composition on cyclohexanone conversion, selectivity towards cyclohexanone oxime as well as  $\text{H}_2$  conversion and the leaching of Pd from the catalyst during the reaction.





**Figure 4.5.** The effect of solvent composition on the ammoximation of cyclohexanone.

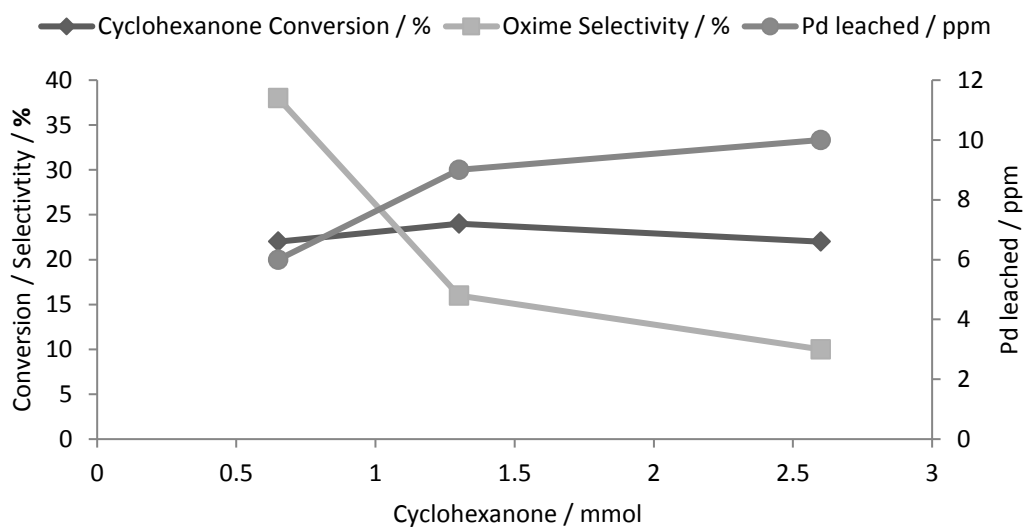
**Reaction conditions:** 5 wt. % Pd / TS-1 (0.05 g), cyclohexanone (0.13 g), NH<sub>3</sub> (0.08 g, 28 wt. %), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 90 min, total solvent mass 8.5 g, 80 °C.

It can be observed that in a pure H<sub>2</sub>O system rates of cyclohexanone conversion are extremely high, 73 %, while no oxime is observed. This can be explained when the amount of Pd leached from the support is considered. A pure H<sub>2</sub>O solvent system results in a high amount of leaching of Pd into the solvent (115 ppm). It has been shown by Lunsford and co-workers<sup>28</sup> that colloidal Pd is active for the direct synthesis of H<sub>2</sub>O<sub>2</sub>. As Pd is present in the solution it is suggested that diffusion of reactant gas to those active sites responsible for H<sub>2</sub>O<sub>2</sub> synthesis present on the unsupported Pd is quicker than diffusion to Pd supported on TS-1. H<sub>2</sub>O<sub>2</sub> formed by colloidal Pd will have a greater diffusion pathway to Ti(IV) sites present on the support than that formed by supported Pd. This increased diffusion pathway means that decomposition of H<sub>2</sub>O<sub>2</sub>, due to high temperatures and presence of NH<sub>3</sub> as well as catalytic breakdown of H<sub>2</sub>O<sub>2</sub> may be greater than when H<sub>2</sub>O<sub>2</sub> is synthesised by supported Pd.

When a pure t-BuOH solvent system is utilised conversion of cyclohexanone is 74 % while selectivity to the oxime is very low (6 %), while measurement of H<sub>2</sub> conversion shows that in a 100 % t-BuOH system H<sub>2</sub> conversion is high (78 %). It is believed that the solubility of H<sub>2</sub> is much higher than that of O<sub>2</sub> and so conversion of cyclohexanone to the corresponding alcohol by hydrogenation is high accounting for both the high conversion and low selectivity rates. Furthermore another reason for the low selectivity towards cyclohexanone oxime may be due to an increase in the hydrogenation of H<sub>2</sub>O<sub>2</sub>, as H<sub>2</sub> availability is increased. It is therefore suggested that by manipulation of the solvent system it would be possible to optimise H<sub>2</sub> : O<sub>2</sub> ratio in a manner that improves selectivity towards cyclohexanone oxime.

#### 4.3.4. Cyclohexanone concentration optimization.

It has been shown above that it is possible to synthesise  $\text{H}_2\text{O}_2$  in the presence of cyclohexanone from  $\text{H}_2$  and  $\text{O}_2$  in a  $\text{H}_2\text{O}$  / t-BuOH solvent mixture. However catalytic activity decreased slightly upon incorporation of cyclohexanone. Figure 4.6 shows the effect of cyclohexanone concentration on conversion of cyclohexanone and selectivity towards the oxime.



**Figure 4.6.** The effect of cyclohexanone concentration on the ammoximation of cyclohexanone. **Reaction conditions:** 5 wt. % Pd / TS-1 (0.05 g), cyclohexanone (X g),  $\text{NH}_3$  (0.08 g, 28 wt. %, 1.3 mmol), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 90 min, 5.6 g t-BuOH + 2.69 g  $\text{H}_2\text{O}$  (66 wt. % t-BuOH), 80 °C.

It is observed that as cyclohexanone concentration increases selectivity towards the oxime decreases, from 38 to 10 % as cyclohexanone concentration rises from 0.65 to 2.6 mmol. There is little change in conversion of cyclohexanone with increasing concentration of this reactant, with conversion remaining in the range of 22 – 26 % regardless of concentration. It can also be observed that as cyclohexanone concentration increases the amount of Pd leached from the catalyst increases, suggesting that it is not just the presence of  $\text{H}_2\text{O}$  in the system that can contribute to the loss of catalyst stability, although Pd leaching is observed to be much less than that observed when a  $\text{H}_2\text{O}$  only solvent is utilised, with only 10 ppm of Pd detected. Further work investigating methods to increase catalyst stability is investigated in Chapter 5.

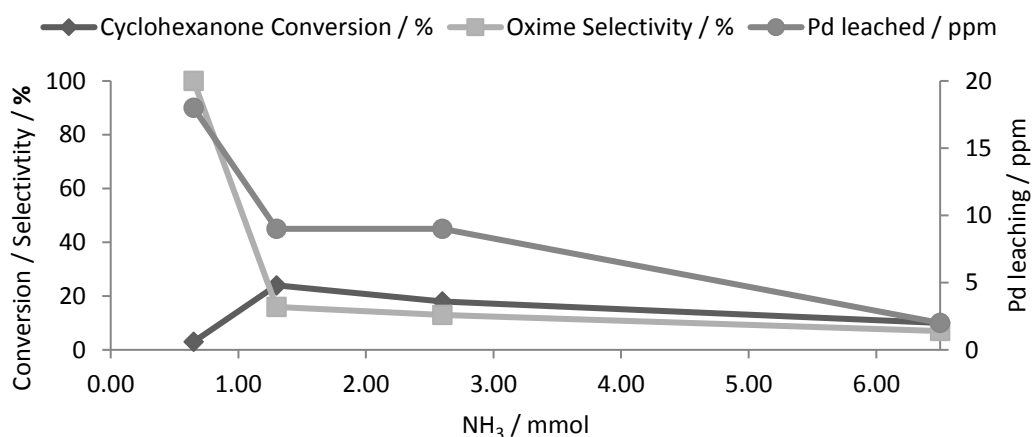
It can be assumed that not all  $\text{H}_2$  present in the system (approximately 1.3 mmol) is converted to  $\text{H}_2\text{O}_2$  and it has been shown above that reaction conditions can cause  $\text{H}_2\text{O}_2$  degradation. This means that  $\text{H}_2\text{O}_2$  concentration within the system may be much lower than that of  $\text{NH}_3$

and cyclohexanone. The selectivity towards cyclohexanone oxime, during the ammoximation reaction, when pre-formed  $\text{H}_2\text{O}_2$  is added to the reaction mixture has been shown to be linked to the ratio of reactants ( $\text{H}_2\text{O}_2$  :  $\text{NH}_3$  : cyclohexanone) and it has been observed that a 1 : 1 : 1 ratio is optimal<sup>23</sup>. If this is true for the ammoximation process via *in-situ*  $\text{H}_2\text{O}_2$  synthesis lowering the cyclohexanone concentration may cause the concentration of cyclohexanone to become similar to that of  $\text{H}_2\text{O}_2$  and in turn results in an improved selectivity.

#### 4.3.5. Ammonia concentration optimization.

It is well known that the presence of basic conditions leads to rapid degradation of  $\text{H}_2\text{O}_2$ <sup>29</sup>. This offers a particular challenge to the synthesis of cyclohexanone oxime via the *in-situ* synthesis of  $\text{H}_2\text{O}_2$ , especially when considering the high temperatures required for significant oxime formation, which also presents issues to  $\text{H}_2\text{O}_2$  stability. The formation of hydroxylamine is believed to require  $\text{H}_2\text{O}_2$  co-ordination to the Ti (IV) sites of TS-1, however the highly basic conditions within the reaction solution, as well as high temperature, means that  $\text{H}_2\text{O}_2$  degradation is a considerable issue and that not all the  $\text{H}_2\text{O}_2$  formed is able to diffuse to the Ti (IV) sites on the support without undergoing degradation to  $\text{H}_2\text{O}$ .

Figure 4.7 shows the effect of  $\text{NH}_3$  concentration on conversion of cyclohexanone and selectivity towards the oxime.



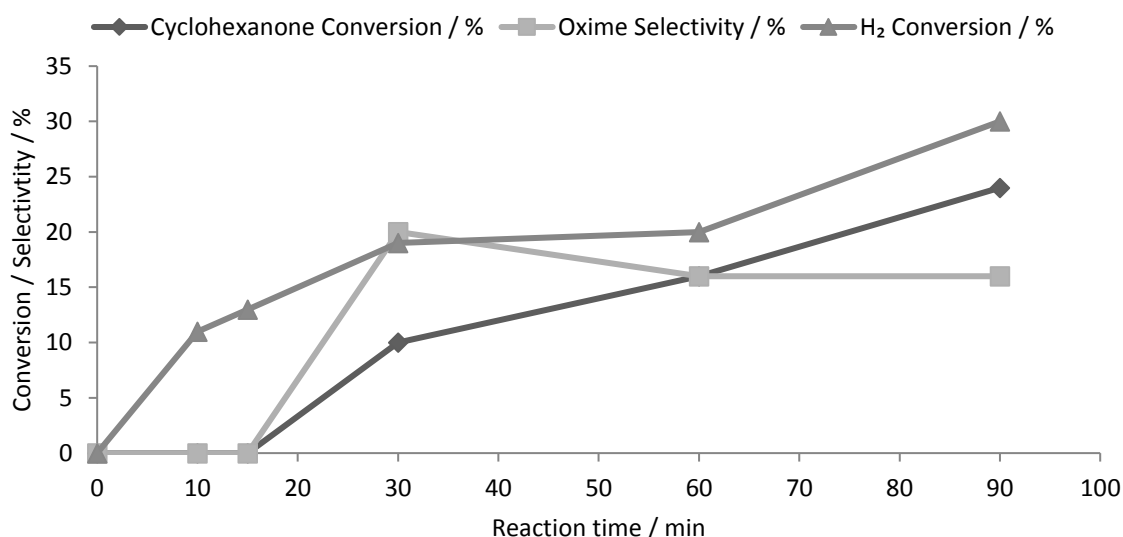
**Figure 4.7.** The effect of ammonia concentration on the ammoximation of cyclohexanone.

**Reaction conditions:** 5 wt. % Pd / TS-1 (0.05 g), cyclohexanone (0.13 g, 1.3 mmol),  $\text{NH}_3$  (X g, 28 wt. %), total pressure 580 psi,  $\text{H}_2$  /  $\text{O}_2$  = 0.525, 1200 rpm, 90 min, 5.6 g t-BuOH + 2.69 g  $\text{H}_2\text{O}$  (66 wt. % t-BuOH), 80 °C.

It can be seen that selectivity towards the oxime decrease as  $\text{NH}_3$  concentration rises, from 100 to 7 %. This decrease is unsurprising, as previously discussed the presence of  $\text{NH}_3$  in the reaction solution is detrimental to  $\text{H}_2\text{O}_2$ , as  $\text{H}_2\text{O}_2$  is stabilised by the presence of acidic reaction conditions. With more  $\text{NH}_3$  in the reaction solution it is likely that rates of  $\text{H}_2\text{O}_2$  degradation will increase due to the higher pH of the solution. It has previously been shown in Section 4.2.2 above that no  $\text{H}_2\text{O}_2$  is detected when catalyst activity towards  $\text{H}_2\text{O}_2$  synthesis in the presence of  $\text{NH}_3$  is investigated. However this does not mean that no  $\text{H}_2\text{O}_2$  is formed, and the detection of cyclohexanone oxime indicates that  $\text{H}_2\text{O}_2$  is indeed formed. Interestingly the amount of Pd leached from the support decreases with increasing  $\text{NH}_3$  concentration, from 18 to 2 ppm. It is suggested that as some  $\text{H}_2\text{O}$  from the reaction solution is replaced with  $\text{NH}_3$  it is possible this contributes to some reduction in the overall leaching of Pd from the catalyst.

#### 4.3.6. Reaction time optimisation.

Figure 4.8 shows the effect of reaction time on the ammoximation of cyclohexanone. It should be noted that reactions were performed for varied durations of time rather than sampling from a continuous experiment and this would affect the reaction dynamics.



**Figure 4.8.** The effect of reaction time on the ammoximation of cyclohexanone.

**Reaction conditions:** 5 wt. % Pd / TS-1 (0.05 g), cyclohexanone (0.13 g),  $\text{NH}_3$  (0.08 g, 28 wt. %), total pressure 580 psi,  $\text{H}_2/\text{O}_2 = 0.525$ , 1200 rpm, X min, 5.6 g t-BuOH + 2.69 g  $\text{H}_2\text{O}$  (66 wt. % t-BuOH), 80 °C.

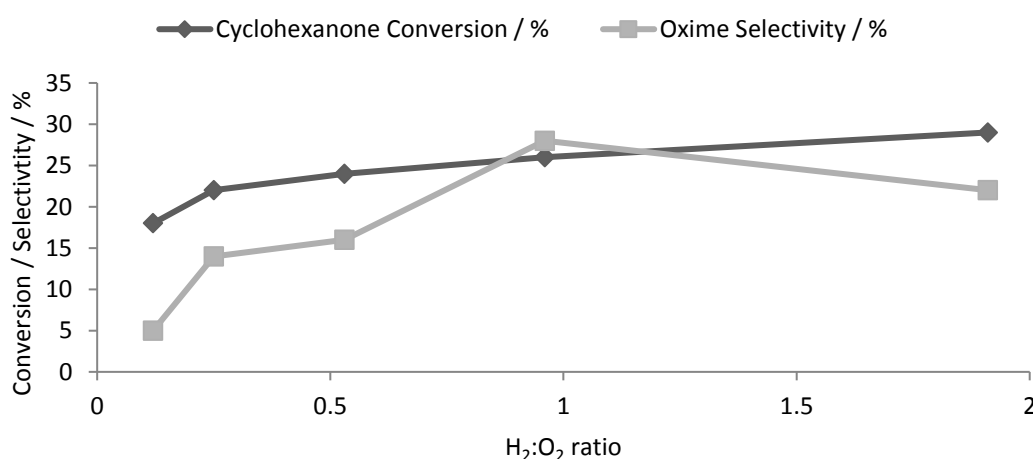
As can be seen an induction period is required for any oxime to be detected. Even though  $\text{H}_2$  conversion is measured at 13 % at a reaction time of 15 min no oxime is detected. It is

suggested that at short reaction times the concentration of  $\text{H}_2\text{O}_2$  synthesised is minor and the degradation of  $\text{H}_2\text{O}_2$  due to reaction conditions ensures that no  $\text{H}_2\text{O}_2$  is able to diffuse to the Ti(IV) sites present on the support to result in the formation of cyclohexanone oxime. It may also be possible that a proportion of  $\text{NH}_3$  is removed from the system while the reaction is reaching reaction temperature. The formation of  $(\text{NH}_4)_2\text{CO}_3$  or  $\text{NH}_4\text{HCO}_3$ , through reaction between the  $\text{CO}_2$ , used as a diluent for the reactant gasses, and  $\text{NH}_3$  may contribute to the lack of oxime detected at short reaction times. It may be that the lack of oxime formation is due to the unavailability of a proportion of  $\text{NH}_3$ . It is not until the ammonia salt decomposes and the  $\text{NH}_3$  is free to produce hydroxylamine that the oxime can be formed.

It is observed that as reaction time increases so does the conversion of cyclohexanone, to a maximum of 24 % at a reaction time of 90 mins. As with cyclohexanone conversion the conversion of  $\text{H}_2$  increases with time to a maximum of 30 % at a reaction time of 90 mins. Selectivity remains stable between a reaction time of 30 and 90 minutes, at approximately 20 %. Although this is a relatively low value it is suggested that through catalyst design it is possible to improve selectivity as well as conversion and this is discussed in Chapter 5.

#### 4.3.7. Reactant gas composition optimization.

The effect that the ratio of  $\text{H}_2 : \text{O}_2$  has on the ammoxidation of cyclohexanone is shown in Figure 4.9.



**Figure 4.9.** The effect of  $\text{H}_2:\text{O}_2$  ratio on the ammoxidation of cyclohexanone, while maintaining total pressure. **Reaction conditions:** 5 wt. % Pd / TS-1 (0.05 g), cyclohexanone (0.13 g),  $\text{NH}_3$  (0.08g, 28 wt. %), total pressure 580 psi, 1200 rpm, 90 min, 5.6 g t-BuOH + 2.69 g  $\text{H}_2\text{O}$  (66 wt. % t-BuOH), 80 °C.

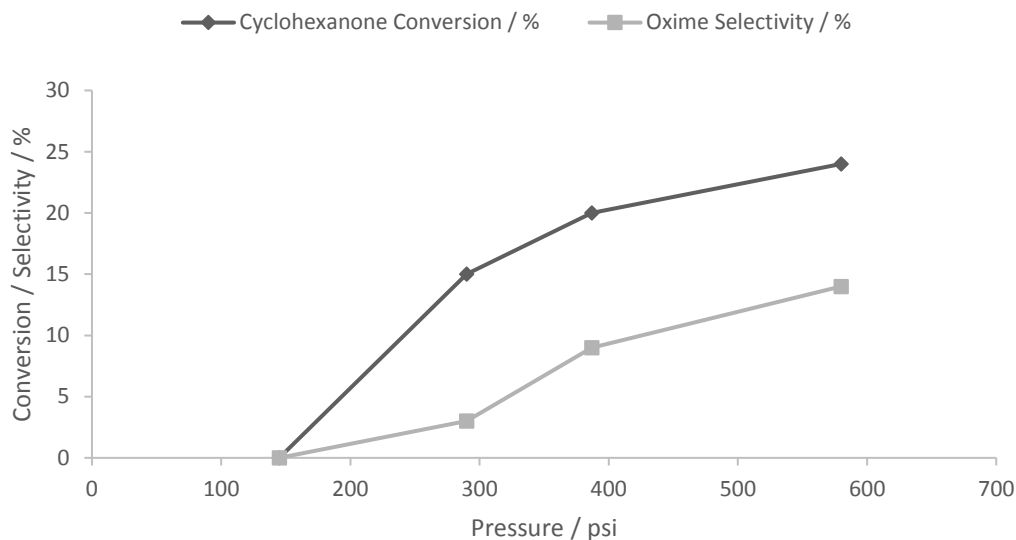
Hutchings and co-workers have shown that the optimal ratio of  $H_2 : O_2$  for the direct synthesis of  $H_2O_2$ , under their reaction conditions, in a  $H_2O$  -  $MeOH$  solvent system is 1 : 2 in favour of  $O_2$ <sup>9, 13, 16</sup>. It was theorised that the high hydrogenation activity of Pd would mean that the use of lower  $H_2$  pressures would result in less hydrogenation of cyclohexanone to unwanted by-products, such as cyclohexanol, and in turn greater selectivity towards the oxime.

However this was not observed, as can be seen in Figure 4.9 selectivity towards cyclohexanone oxime remains fairly low when an excess of  $O_2$  is present selectivity is particularly low, with selectivity towards the oxime observed to reach a minimum of 5 % when a  $H_2 : O_2$  ratio of 1 : 8 is utilised. It is suggested that at low  $H_2$  content little  $H_2O_2$  is synthesised and so the formation of the oxime is limited. However it has been shown that cyclohexanone is able to undergo homogeneous reaction to produce cyclohexenylcyclohexanone and cyclohexanone azine and it is suggested that at low  $H_2O_2$  synthesis rates the propensity of these homogeneous reactions to occur increases and so low catalytic selectivity is observed.

As the ratio of reactant gases becomes close to 1 : 1 selectivity towards the oxime increases and peaks at 28 %. It is suggested that at this ratio catalytic selectivity towards  $H_2O_2$  is greatest and in turn the net rate of  $H_2O_2$  synthesis is greatest. Beyond a 1:1 ratio, selectivity towards the oxime decreases to 22%, while conversion continues to rise. It is suggested that the excess  $H_2$ , in the presence of a hydrogenation catalyst such as Pd, leads to unwanted formation of cyclohexanol as well as other unwanted by-products when  $H_2$  is present at a high concentration. It is also likely that the contribution towards  $H_2O_2$  degradation from hydrogenation, rather than decomposition, is higher and it is possible that the net  $H_2O_2$  synthesis rate decreases allowing for an increase in the formation of cyclohexenylcyclohexanone and cyclohexanone azine.

#### 4.3.8. Total reactant gas pressure, while maintaining H<sub>2</sub> : O<sub>2</sub>.

Figure 4.10 shows the effect of total gas pressure on the ammoximation of cyclohexanone, while maintaining H<sub>2</sub> : O<sub>2</sub> at 1 : 2.



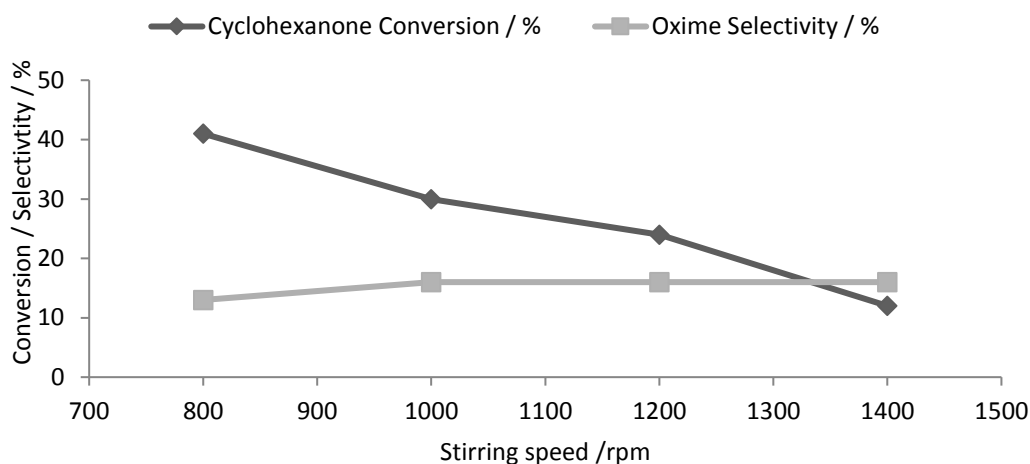
**Figure 4.10.** The effect of total reactant gas pressure, while maintaining H<sub>2</sub> : O<sub>2</sub>, on the ammoximation of cyclohexanone.

**Reaction conditions:** 5 wt. % Pd / TS-1 (0.05 g), cyclohexanone (0.13 g, 1.3 mmol), NH<sub>3</sub> (0.08 g, 28 wt. %), total pressure X psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 90 min, 5.6 g t-BuOH + 2.69 g H<sub>2</sub>O (66 wt. % t-BuOH), 80 °C.

It is observed that as total pressure rises both cyclohexanone conversion and oxime selectivity increases. By increasing total pressure more H<sub>2</sub> and O<sub>2</sub> dissolves in the solvent and so the total concentration of H<sub>2</sub>O<sub>2</sub> produced is likely to increase with total reactant gas pressure. This in turn leads to an increase in the formation of NH<sub>2</sub>OH and conversion of cyclohexanone to the oxime. At low pressures of reactant gas, it is likely that some H<sub>2</sub>O<sub>2</sub> will be formed, however the reaction conditions used mean that H<sub>2</sub>O<sub>2</sub> degradation is high and subsequently NH<sub>2</sub>OH formation is low. This may explain why no oxime is detected when a total gas pressure of 145 psi is utilised. As total pressure rises both the selectivity towards the oxime and the conversion of cyclohexanone, to 14 and 24 % for selectivity and conversion respectively when a total pressure of 580 psi is applied.

#### 4.3.9. Stirring speed optimization.

Figure 4.11 shows the effect of stirring speed on the ammoximation of cyclohexanone.



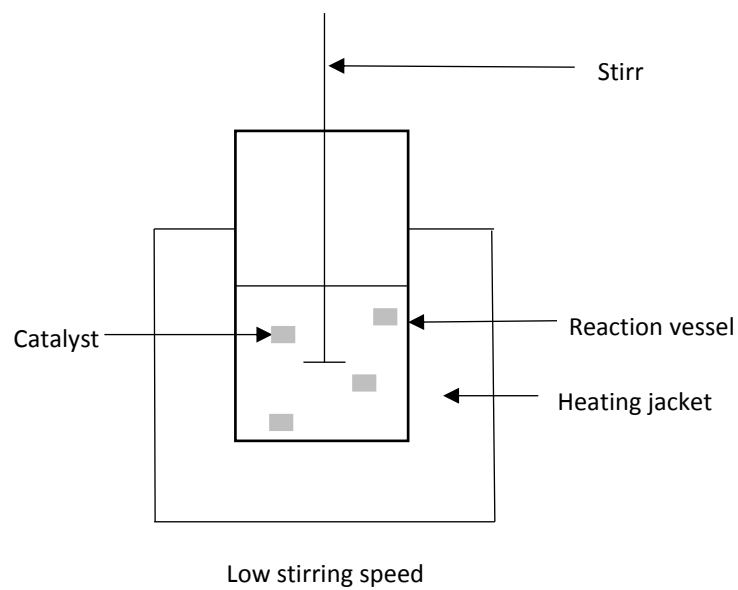
**Figure 4.11.** The effect of stirring speed on the ammoximation of cyclohexanone.

**Reaction conditions:** 5 wt. % Pd / TS-1 (0.05 g), cyclohexanone (0.13 g),  $\text{NH}_3$  (0.08 g, 28 wt. %), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , X rpm, 90 min, 5.6 g t-BuOH + 2.69 g  $\text{H}_2\text{O}$  (66 wt. % t-BuOH), 80 °C.

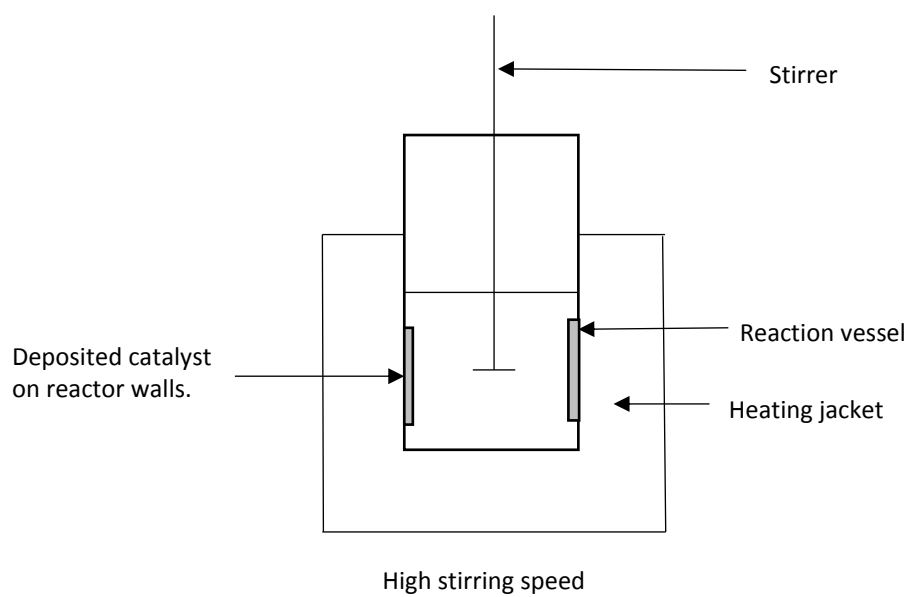
As can be seen in Figure 4.11 conversion of cyclohexanone to the oxime decreases with stirring speed. It was initially believed that improving stirring speed would cause greater dissolution of the reactant gasses and in turn be beneficial to enhancing  $\text{H}_2\text{O}_2$  concentration. If this was the case it would be expected that both cyclohexanone conversion and selectivity towards the oxime would improve. Instead very little change in selectivity is observed, while conversion of cyclohexanone decreases dramatically, from 41 to 12 % as stirring speed increases from 800 to 1400 rpm.

It may be that the decrease in conversion is a result of the catalyst being forced onto the wall of the reactor liner at higher speeds, in a manner similar to that seen in Figures 4.12 and 4.13. This would result in a decrease in the availability of the active sites responsible for the direct synthesis of  $\text{H}_2\text{O}_2$  and in turn formation of the hydroxylamine intermediate decreases. As hydroxylamine is utilised in the formation of cyclohexanone oxime it is possible to use the yield of cyclohexanone oxime as an indication of the concentration of hydroxylamine produced through the course of a reaction.





**Figure 4.12.** The effect of low reactor speed on catalyst distribution in a sealed autoclave.



**Figure 4.13.** The effect of high reactor speed on catalyst distribution in a sealed autoclave.

#### 4.4. Determining the activity of leached metal towards the ammoximation of cyclohexanone via *in-situ* synthesis of $\text{H}_2\text{O}_2$ .

It has previously been determined in Sections 4.3.4 and 4.3.6 that leaching of Pd from the support can be a significant issue and is one that must be addressed through catalyst and process design. To determine the activity of the leached metal towards the ammoximation of cyclohexanone a hot filtration was carried out, the procedure for which is outlined in Chapter 2 Section 2.3.8. but is briefly discussed below. Finally the activity of 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  when used in addition to TS-1, as a physical mixture, towards the ammoximation of cyclohexanone was investigated.

Due to the reactor availability the hot filtration reaction was carried out in a 100 ml stainless steel Parr autoclave in comparison all previous data was determined using a 50 ml stainless steel Parr autoclave.

After a standard reaction the catalyst is removed by filtration, the reactor cleaned to ensure no contamination and the filtrate returned to the reactor, which is re-pressurised with reactant gas (5%  $\text{H}_2$  /  $\text{CO}_2$  and 25 %  $\text{O}_2$  /  $\text{CO}_2$ ) and allowed to come to the desired temperature (80 °C). The reaction is allowed to run for a further 0.5 h after which the reactor is cooled to room temperature and analysis of the reaction solution and reactant gas is carried out as outlined in Chapter 2 Section 2.3.8. Table 4.5 shows the results of this study for a 5 wt. % Pd / TS-1 catalyst.

**Table 4.5.** The activity of leached Pd on the ammoximation of cyclohexanone.

	Cyclohexanone Conversion / %	Oxime Selectivity / %	Oxime Yield / %	H <sub>2</sub> Conversion / %	Pd leached / ppm
Catalyst present <sup>a</sup>	20	42	8	36	11
Filtrate <sup>b</sup>	23	35	8	6	11
Filtrate + TS-1 <sup>c</sup>	22	37	8	8	11
Au-Pd / TiO <sub>2</sub> + TS-1 <sup>d</sup>	3	0	0	25	6

<sup>a</sup> **Reaction conditions:** 5 wt. % Pd / TS-1 (0.05 g), cyclohexanone (0.13 g, 1.3 mmol), NH<sub>3</sub> (0.08 g, 28 wt. %, 1.3 mmol), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 90 min, 5.6 g t-BuOH + 2.69 g H<sub>2</sub>O (66 Wt. % t-BuOH), 80 °C.

<sup>b</sup> **Reaction conditions:** Cyclohexanone (0.13 g, 1.3 mmol), NH<sub>3</sub> (0.08 g, 28 wt. %, 1.3 mmol), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g H<sub>2</sub>O (66 wt. % t-BuOH), 80 °C.

<sup>c</sup> **Reaction conditions:** TS-1 (0.05 g), Cyclohexanone (0.13 g, 1.3 mmol), NH<sub>3</sub> (0.08 g, 28 wt. %, 1.3 mmol), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g H<sub>2</sub>O (66 wt. % t-BuOH), 80 °C.

<sup>d</sup> **Reaction conditions:** 2.5 wt. % Au – 2.5 wt.% Pd / TiO<sub>2</sub> (0.05 g), TS-1 (0.05 g), Cyclohexanone (0.13 g, 1.3 mmol), NH<sub>3</sub> (0.08 g, 28 wt. %, 1.3 mmol), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g H<sub>2</sub>O (66 wt. % t-BuOH), 80 °C.

Investigation into the activity of a 5 wt. % Pd / TS-1 catalyst towards the ammoximation of cyclohexanone is observed to result in an oxime yield of 8 %. It has been found that after the reaction 11 ppm of leached Pd is detected in the reaction solution. Investigation into the activity of the filtrate (with the catalyst removed) shows no additional formation of the oxime suggesting that leached Pd has no activity towards the ammoximation of cyclohexanone. However cyclohexanone conversion is observed to increase from 20 to 23 % it is suggested that the increase in cyclohexanone conversion may be a result of hydrogenation of cyclohexanone to cyclohexanol or uncatalysed homogeneous side reactions of cyclohexanone, as reported by Cesana *et.al.*<sup>8</sup> It is observed that upon investigation of the filtrate there is some H<sub>2</sub> conversion (6 %) this may be attributed to one or combination of the following possibilities; the formation of H<sub>2</sub>O<sub>2</sub>, hydrogenation of cyclohexanone or error in analysis of the reactant gas post reaction by gas chromatography. It is suggested that if any H<sub>2</sub>O<sub>2</sub> is formed by the homogeneous Pd it is unable to diffuse to the Ti (IV) sites present on the support and be involved in the formation of hydroxylamine.

Further investigation into the activity of the leached Pd towards the ammoximation of cyclohexanone was conducted, with the addition of bare TS-1 to the filtrate. It is observed that again there is no activity towards the formation of cyclohexanone oxime. However an

increase in cyclohexanone conversion is observed from 20 to 22 %, as is some H<sub>2</sub> conversion (8 %). This suggests that again there may be some homogeneous side reactions of cyclohexanone or hydrogenation of cyclohexanone.

Finally it was decided to determine the activity of 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> when used in addition to TS-1 towards the ammoximation of cyclohexanone. It can be seen that there is no oxime produced from this physical mixture, despite some conversion of cyclohexanone (3 %), this is attributed to the hydrogenation of cyclohexanone to cyclohexanol or uncatalysed homogeneous side reactions of cyclohexanone. It is known that 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> is active towards the direct synthesis of H<sub>2</sub>O<sub>2</sub>, as shown in Table 4.1. It has further been shown that for a 5 wt. % Pd / TS-1 catalyst there is an improvement in catalytic activity towards the direct synthesis of H<sub>2</sub>O<sub>2</sub> when using a t-BuOH / water solvent mixture in comparison to a MeOH / water solvent, as seen in Table 4.2. It is therefore suggested that an improvement in catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis may also be observed for the 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> catalyst, when using a t-BuOH / water solvent. It is suggested that the lack of oxime formation is due to the degradation of H<sub>2</sub>O<sub>2</sub> as it diffuses from the 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> catalyst to the Ti (IV) sites on the TS-1.

As such future investigation into catalyst design will focus on the use of TS-1 supported catalysts.

## 4.5. Conclusion.

In this Chapter it has been shown that the impregnation of Au, Pd and Au-Pd onto a commercial TS-1 results in the production of catalysts that are active towards  $\text{H}_2\text{O}_2$  synthesis at sub-ambient temperatures. As seen in Table 4.6 productivity values of 5 wt. % Pd / TS-1 are observed to be greater than the bi-metallic 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 catalyst. This trend is inconsistent with previous work conducted by Hutchings and co-workers who have observed a synergistic effect when both Au and Pd are supported on a variety of supports including  $\text{TiO}_2$ <sup>13</sup>,  $\text{SiO}_2$ <sup>14</sup> and carbon<sup>14</sup>. Possibly this is due to the extent of alloying between Au and Pd when utilising TS-1 as a support. This is investigated further in Chapter 5. Interestingly the 5 wt. % Pd / TS-1 catalyst is seen to offer much greater productivity values than a number of bi-metallic Au-Pd catalysts including 2.5 wt. % Au - 2.5 wt. % Pd /  $\text{TiO}_2$  and shows similar activity towards  $\text{H}_2\text{O}_2$  synthesis as 2.5 wt. % Au - 2.5 wt. % Pd / C.

**Table 4.6.** Comparison of catalytic activity towards  $\text{H}_2\text{O}_2$  synthesis.

Catalyst	Productivity / $\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$
5 wt. % Au / TS-1	2
2.5 % Au – 2.5 wt. % Pd / TS-1	100
5 wt. % Pd / TS-1	116
5 wt. % Au / $\text{TiO}_2$	7
2.5 % Au – 2.5 wt. % Pd / $\text{TiO}_2$	64
5 wt. % Pd / $\text{TiO}_2$	30
5 wt. % Au / C	1
2.5 % Au – 2.5 wt. % Pd / C	110
5 wt. % Pd / C	55

**Reaction conditions:** Catalyst (0.01 g), 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 5.6 g MeOH + 2.9 g  $\text{H}_2\text{O}$  (66 Wt. %  $\text{CH}_3\text{OH}$ ), 2 °C.

Further investigation into the activity of 5 wt. % Pd / TS-1 utilising a water - alcohol solvent system shows that when t-BuOH is utilised as the solvent in a 2 : 1 ratio with water a greater productivity is observed when compared to a MeOH – water solvent system, at 30 °C. The productivity of the 5 wt. % Pd / TS-1 catalyst is observed to be 60 and 26  $\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$  for a t-BuOH – water and MeOH – water solvent system and this is ascribed to increased  $\text{H}_2$  solubility in t-BuOH compared to MeOH.

The use of elevated temperatures has been shown to be deleterious towards  $\text{H}_2\text{O}_2$  stability when using a water-methanol solvent system, as outlined in Section 4.2.1. It is observed that catalyst activity decreases from 116 to 26  $\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$  for the 5 wt. % Pd / TS-1 catalyst and this is attributed to an increase in the degradation of  $\text{H}_2\text{O}_2$  via hydrogenation, although this hypothesis must be investigated further. In addition the presence of basic conditions, *i.e.*  $\text{NH}_3$ , has been shown to result in the total degradation of highly concentrated  $\text{H}_2\text{O}_2$  (12 wt.%) when using a water-t-butanol solvent system. However it is not possible to determine if the decrease in  $\text{H}_2\text{O}_2$  concentration is a result of  $\text{H}_2\text{O}_2$  degradation or the formation of hydroxylamine. It may be of interest to determine the extent of hydroxylamine produced and it is suggested that quantification may be possible through the addition of cyclohexanone and determination of the yield of cyclohexanone oxime. However, the conditions utilised for the ammoximation of cyclohexanone to cyclohexanone oxime are considered to be harsh towards  $\text{H}_2\text{O}_2$  stability, in particular the presence of base and the utilisation of elevated temperatures as such in the absence of the catalyst it is suggested that total degradation of  $\text{H}_2\text{O}_2$  will occur.

Further investigation into the activity of Au, Pd and Au-Pd supported TS-1 catalysts towards the ammoximation of cyclohexanone to cyclohexanone oxime in the presence of pre-formed  $\text{H}_2\text{O}_2$  has shown that the impregnation of Au and Pd does not adversely affect the activity of the catalyst towards the ammoximation of cyclohexanone. The monometallic Au catalyst supported on TS-1 provides a similar yield of cyclohexanone oxime as the bare TS-1 support (28 %), while the monometallic 5 wt. % Pd / TS-1 and 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 catalysts are observed to offer a slightly smaller yield of cyclohexanone oxime, with a yield of 23 % observed for both the Pd / TS-1 and Au-Pd / TS-1 catalysts as shown in Table 4.7.

**Table 4.7.** Comparison of catalytic activity towards the ammoximation of cyclohexanone via the addition of pre-formed  $\text{H}_2\text{O}_2$ .

Catalyst	Cyclohexanone oxime yield / %
TS-1	28
5 wt. % Au / TS-1	28
2.5 wt. % Au – 2.5 wt. % Pd / TS-1	23
5 wt. % Pd / TS-1	23

**Reaction Conditions:** Catalyst (0.05 g), cyclohexanone (10 mmol),  $\text{NH}_3$  (28 wt. % 12 mmol),  $\text{H}_2\text{O}$  (2.5 g), t-BuOH (2.5 g), 80 °C, 35 wt. %  $\text{H}_2\text{O}_2$  (10 mmol, 0.89  $\text{mlhr}^{-1}$  then 0.5 h stir).

It is shown through the formation of the oxime that  $\text{H}_2\text{O}_2$  synthesis is possible under these conditions even though  $\text{H}_2\text{O}_2$  stability may be an issue. The ability to produce cyclohexanone oxime via *in-situ*  $\text{H}_2\text{O}_2$  synthesis may open up a number of other oxidation processes that involve TS-1 and preformed  $\text{H}_2\text{O}_2$  to this one pot approach, in particular the ammoximation of other ketones.

Reaction conditions have been investigated and optimised for the ammoximation of cyclohexanone using a model 5 wt. % Pd / TS-1 catalyst. It has been shown that the utilisation of increased reaction temperatures in particular is a key requirement to improve yield of cyclohexanone oxime, with oxime yield increasing from 0 to 10 % as reaction temperature increases from 30 to 120 °C. This is in agreement with the work of Wu *et.al*<sup>18</sup>. who have report that increasing reaction temperature results in an increase in an increased yield of cyclohexanone oxime. Furthermore it is observed that by improving  $\text{H}_2$  solubility, through manipulation of reactant gas ratios (Section 4.3.8), total reactant gas pressure (Section 4.3.9) and solvent composition (Section 4.3.4) it is possible to improve yield of cyclohexanone oxime. It is suggested that by increasing  $\text{H}_2$  solubility it is possible to ensure that the rates of  $\text{H}_2\text{O}_2$  synthesis and hydroxylamine formation are similar and oxime yield is improved.

The improved cyclohexanone oxime yield at temperatures considered detrimental towards  $\text{H}_2\text{O}_2$  stability suggests that rate of hydroxylamine formation is much greater than that of  $\text{H}_2\text{O}_2$  degradation. It is suggested that investigation into the rates of these two reactions form the basis of further study.

Finally it is observed that the activity of leached metal towards the ammoximation of cyclohexanone is minimal, with no additional formation of cyclohexanone oxime upon removal of the heterogeneous catalyst. It is suggested that the reaction conditions utilised (80 °C and presence of basic reaction conditions) result in the degradation of  $\text{H}_2\text{O}_2$  synthesised by homogeneous Pd before it is able to be activated by the Ti(IV) sites present on the TS-1 support. As such any  $\text{H}_2\text{O}_2$  synthesised by the homogeneous Pd is not utilised in the formation of cyclohexanone oxime. Furthermore it has been demonstrated that the physical mixture of a catalyst known to be active towards the direct synthesis of  $\text{H}_2\text{O}_2$  with TS-1 again shows no formation of cyclohexanone oxime and again this is attributed to the degradation of any synthesised  $\text{H}_2\text{O}_2$  before activation by Ti (IV) sites present on the TS-1 support.

It is suggested that the results obtained within this Chapter prove the feasibility of a one-pot approach to the ammoximation of cyclohexanone via *in-situ* H<sub>2</sub>O<sub>2</sub> generation and call for further investigation into the this approach to the synthesis of cyclohexanone oxime.



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## 5. Catalyst Design in the ammoximation of cyclohexanone via the *in-situ* synthesis of H<sub>2</sub>O<sub>2</sub>.

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### 5.1. Introduction.

The previous Chapter outlined the ability of Pd supported on TS-1 to catalyse the ammoximation of cyclohexanone to cyclohexanone oxime, via *in-situ* synthesis of H<sub>2</sub>O<sub>2</sub>. The current Chapter investigates the role of catalyst design in improving selectivity towards cyclohexanone oxime as well as cyclohexanone conversion for this reaction.

Both the role of metal weight loading and heat treatment temperature on catalytic activity towards cyclohexanone formation are explored. Additionally, a variety of supported metal catalysts previously reported as active for direct H<sub>2</sub>O<sub>2</sub> synthesis are now assessed for activity towards the ammoximation of cyclohexanone. Rates of cyclohexanone ammoximation and H<sub>2</sub>O<sub>2</sub> synthesis / degradation are then studied and compared.

In order to screen catalysts efficiently a reaction time of 30 minutes was chosen (unless otherwise stated), other reaction conditions remained consistent with those previously studied in Chapter 4 and are shown for clarity:

Cyclohexanone ammoximation reaction conditions: Catalyst (0.05 g), t-BuOH (5.6 g), H<sub>2</sub>O (2.69 g), cyclohexanone (0.13 g), NH<sub>3</sub> (28 Wt. %, 0.079 g), 5 % H<sub>2</sub> / CO<sub>2</sub> (2.9 MPa) and 25 % O<sub>2</sub>/CO<sub>2</sub> (1.1 MPa), 30 min, 80 °C, 1200 rpm.

H<sub>2</sub>O<sub>2</sub> direct synthesis reaction conditions: Catalyst (0.01 g), MeOH (5.6 g), H<sub>2</sub>O (2.9 g), 5 % H<sub>2</sub> / CO<sub>2</sub> (2.9 MPa) and 25 % O<sub>2</sub> / CO<sub>2</sub> (1.1 MPa), 30min, 2 °C, 1200 rpm.

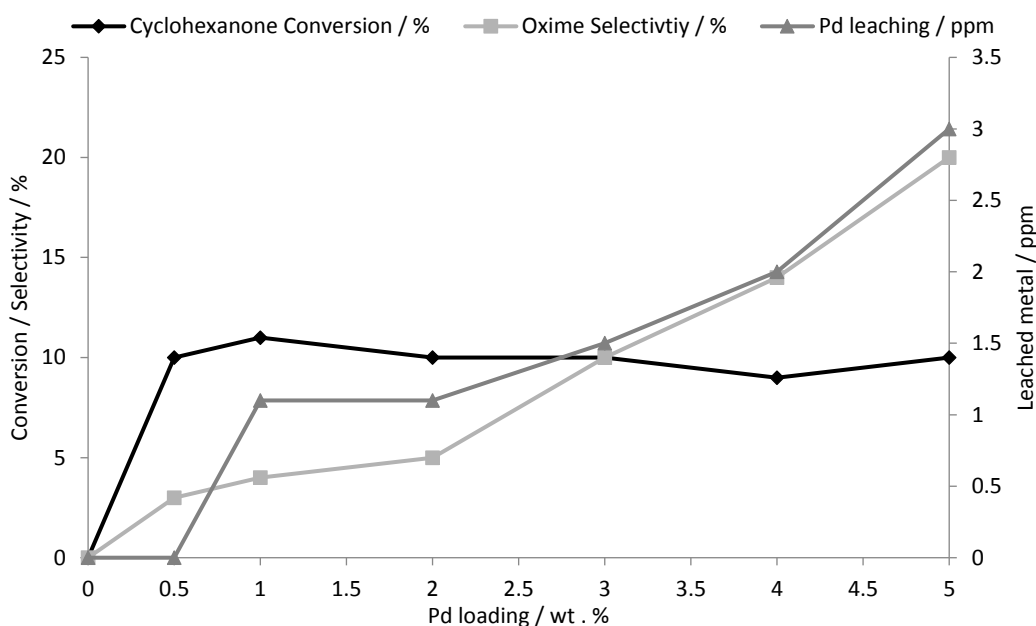
H<sub>2</sub>O<sub>2</sub> degradation reaction conditions: Catalyst (0.01 g), MeOH (5.6 g), H<sub>2</sub>O (2.22 g), H<sub>2</sub>O<sub>2</sub> (50 wt. % 0.68 g), 5 % H<sub>2</sub>/CO<sub>2</sub> (2.9 MPa) 30min, 2 °C, 1200 rpm.

## 5.2. Results and discussion

### 5.2.1. Effect of Pd loading on the ammoximation of cyclohexanone to cyclohexanone oxime via direct synthesis of $\text{H}_2\text{O}_2$ from $\text{H}_2$ and $\text{O}_2$ .

It is well known that Pd is highly active for the direct synthesis of  $\text{H}_2\text{O}_2$  from  $\text{H}_2$  and  $\text{O}_2$ , however it has been reported that Pd is also active towards the subsequent degradation of  $\text{H}_2\text{O}_2$  by hydrogenation to  $\text{H}_2\text{O}$ <sup>1-3</sup>. Thus, catalyst design to improve selectivity towards  $\text{H}_2\text{O}_2$  is considered essential. It is suggested that for a catalyst to be selective towards cyclohexanone oxime whilst also showing high selectivity in  $\text{H}_2$  usage, the rate of  $\text{H}_2\text{O}_2$  synthesis must be similar to that of the ammoximation. This is to ensure that  $\text{H}_2$  is used selectively in oxime formation and not in the formation of  $\text{H}_2\text{O}$ , via  $\text{H}_2\text{O}_2$  degradation.

Figure 5.1 compares the activity of TS-1 supported Pd catalysts towards the ammoximation of cyclohexanone via *in-situ*  $\text{H}_2\text{O}_2$  synthesis.



**Figure 5.1.** The effect of Pd loading on the ammoximation of cyclohexanone.

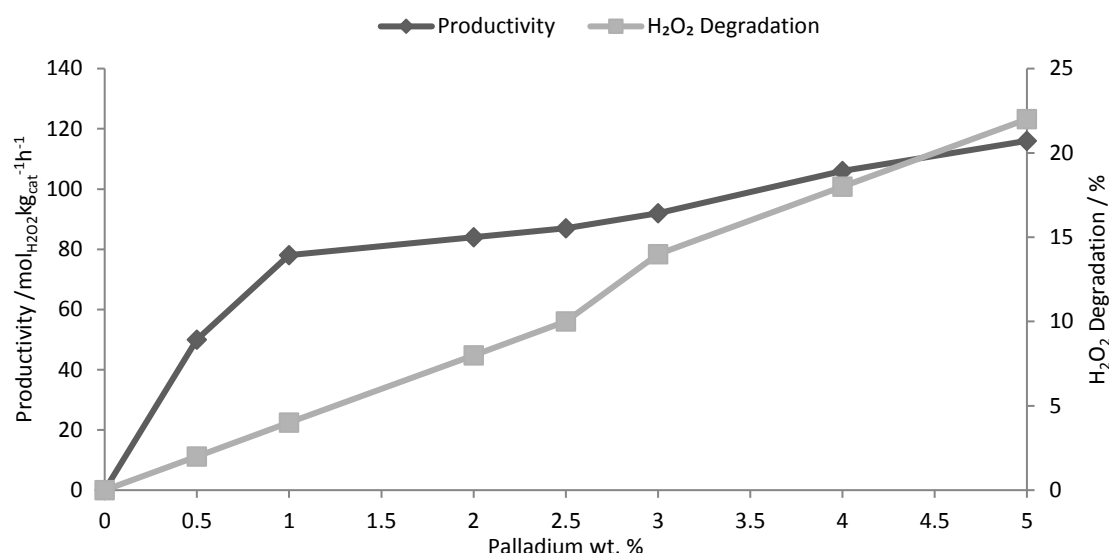
**Reaction conditions:** X wt. % Pd / TS-1 (0.05 g), cyclohexanone (0.13 g, 1.3 mmol),  $\text{NH}_3$  (28 wt. %, 0.08g, 1.3mmol), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g  $\text{H}_2\text{O}$  (66 wt. % t-BuOH), 80 °C.

Firstly, it is observed that the presence of Pd is required to result in the formation of cyclohexanone oxime, no oxime is detected when non-metal supported TS-1 is utilised. It has been reported by Cesena *et.al* that the formation of minor organic by-products, such as cyclohexenylcyclohexanone and cyclohexanone azine can occur through uncatalysed, homogeneous reactions of cyclohexanone. However, it can be observed in Figure 5.1 that in

the absence of Pd, that is when just TS-1 is utilised, no cyclohexanone conversion is measured, over the time period investigated.

It can be observed from Figure 5.1 that there is little change in cyclohexanone conversion, regardless of Pd loading. It is observed that conversion shows low sensitivity to increasing Pd loading over a range of 0.5 – 5 wt. % Pd. On the other hand, oxime selectivity increases greatly with Pd content, from 3 to 20 %, as Pd loading increases from 0.5 to 5 wt. %. The amount of leached Pd correlates well with total metal loading. The 5 wt. % Pd catalyst shows the highest degree of Pd leaching (3 ppm) whilst, no apparent leaching is detected for the 0.5 wt. % Pd catalyst.

To rationalise the trends observed in Figure 5.1, these catalysts were assessed for H<sub>2</sub>O<sub>2</sub> synthesis and degradation under standard conditions, the results of which are shown in Figure 5.2.



**Figure 5.2.** The effect of Pd loading on the direct synthesis and degradation of H<sub>2</sub>O<sub>2</sub>.

**Reaction conditions:** X wt. % Pd / TS-1 (0.01 g), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g MeOH + 2.9 g H<sub>2</sub>O (66 wt. % MeOH), 2 °C.

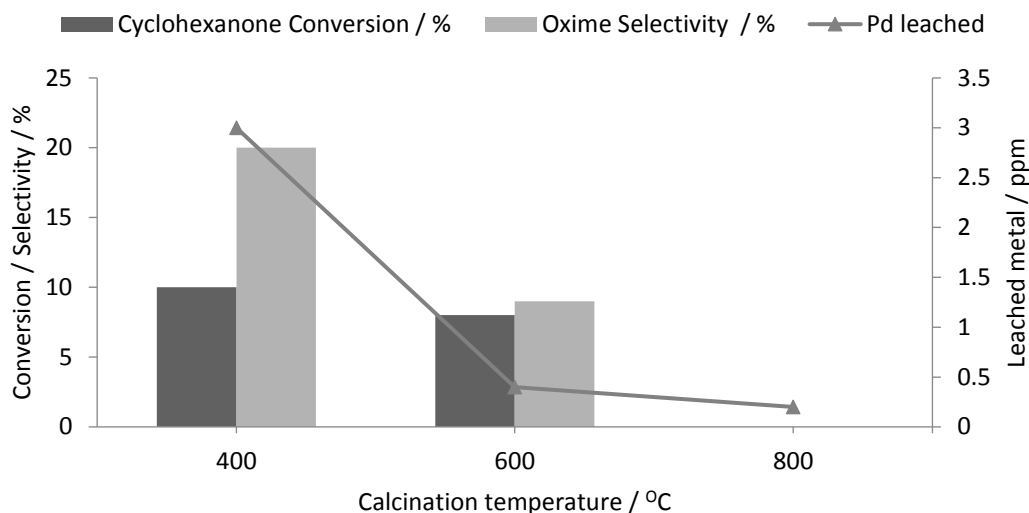
It can be observed that the rates of H<sub>2</sub>O<sub>2</sub> synthesis and degradation increase with Pd loading, with the 5 wt. % Pd / TS-1 offering the greatest productivity (116 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>). The reaction conditions utilised in the ammoximation of cyclohexanone (high reaction temperature of 80 °C and presence of NH<sub>3</sub>) have been shown to result in high H<sub>2</sub>O<sub>2</sub> degradation rates (Chapter 4, Section 4.2.3). It is now possible to conclude that Pd loading also influences activity towards H<sub>2</sub>O<sub>2</sub> degradation, as well as synthesis, although it is considered that the reaction conditions are more significant in this regard.

It is possible to conclude that catalyst activity towards  $\text{H}_2\text{O}_2$  synthesis and degradation, as well as selectivity towards cyclohexanone oxime is dependent on Pd loading. Interestingly the extent of cyclohexanone conversion shows little variation, regardless of Pd loading. However the rate of  $\text{H}_2\text{O}_2$  synthesis is seen to increase as total Pd loading rises. It is possible that the conversion of cyclohexanone may be limited by lack of available  $\text{NH}_3$ . It is suggested that the formation of  $\text{NH}_4\text{HCO}_3$ , through the reaction of  $\text{NH}_3$  and carbonic acid ( $\text{H}_2\text{CO}_3$ ), formed from the  $\text{CO}_2$  reactant gas diluent, results in the removal of  $\text{NH}_3$  from the system. The reaction may therefore be limited by reactant availability. It is suggested that the use of  $\text{N}_2$  as a reactant gas diluent may prevent the formation of  $\text{NH}_4\text{HCO}_3$  and as such overcome this issue.

#### **5.2.2. Effect of calcination temperature on catalyst activity for the ammoximation of cyclohexanone to cyclohexanone oxime via direct synthesis of $\text{H}_2\text{O}_2$ from $\text{H}_2$ and $\text{O}_2$ .**

Previous work by Hutchings and co-workers has shown that calcination of supported Au-Pd catalysts at  $400\text{ }^\circ\text{C}$  in static air produces a stable, re-useable catalyst for the direct synthesis of  $\text{H}_2\text{O}_2$  in a  $\text{H}_2\text{O}$ -MeOH solvent system at  $2\text{ }^\circ\text{C}$  <sup>4</sup>.

As demonstrated in Chapter 4 leaching of supported metals, which are active for  $\text{H}_2\text{O}_2$  synthesis, can be an issue when utilising a solvent system that includes  $\text{H}_2\text{O}$ . In an attempt to produce a more stable and re-usable catalyst the role of calcination temperature on catalyst activity and stability was investigated. 5 wt. % Pd / TS-1 catalysts were calcined (static air, 3 h,  $20\text{ }^\circ\text{C min}^{-1}$  ramp rate) at temperatures ranging from  $400 - 800\text{ }^\circ\text{C}$ . The effect on catalytic activity for the ammoximation of cyclohexanone as well as catalyst stability is shown in Figure 5.3.



**Figure 5.3.** The effect of calcination temperature on the catalytic activity of 5 wt. % Pd / TS-1 towards the ammoximation of cyclohexanone.

**Reaction conditions:** 5 wt. % Pd / TS-1 (0.05 g), cyclohexanone (0.13 g, 1.3 mmol), NH<sub>3</sub> (28 wt. %, 0.08g, 1.3mmol), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g H<sub>2</sub>O (66 wt. % t-BuOH), 80 °C.

It is observed in Figure 5.3 that increasing the calcination temperature from 400 to 800 °C, caused cyclohexanone conversion to decrease from 10 to 0 % and oxime selectivity to fall from 20 to 0 %. Indeed a 3 h calcination in static air, at 800 °C, effectively deactivated the catalyst towards cyclohexanone ammoximation. In contrast with catalyst activity trends, an increase in calcination temperature led to a lower degree of Pd leaching, from 3 and 0.2ppm for calcinations at 400 and 800 °C respectively.

The effect of calcination temperature on the dispersion of Pd was investigated via CO chemisorption, the results of this study are shown in Table 5.1

**Table 5.1.** The effect of calcination temperature on Pd dispersion, as determined by CO chemisorption.

Calcination temperature / °C	Pd Surface area / m <sup>2</sup> g <sup>-1</sup>	Average Crystallite Size / nm	Dispersion / %
400	7.37	23	1.65
600	6.55	26	1.45
800	5.67	31	1.21

It is clear that as calcination temperature increases so the Pd surface area decreases, from 7.73 m<sup>2</sup>g<sup>-1</sup> for the sample calcined at 400 °C to 5.67 m<sup>2</sup>g<sup>-1</sup> for the sample calcined at 800 °C. This coincides with a decrease in dispersion of the metal on the support from 1.65 to 1.21 % and an increase in average crystallite size suggesting that an increase in calcination temperature leads to sintering of the metal nanoparticles. This increase in particle size is

suggested to a significant cause to the loss in catalyst activity towards both the ammoxidation of cyclohexanone and the synthesis of H<sub>2</sub>O<sub>2</sub>.

The effect that calcination temperature has on the crystallinity of the TS-1 support was determined by XRD and the results are shown in Table 5.2. Assigned diffractograms are shown in Appendix 5.1, Figures A1, A2 and A3.

**Table 5.2.** The effect of metal impregnation and calcination temperature upon the physical properties of TS-1 catalysts as determined by XRD and N<sub>2</sub> physisorption.

Catalyst	Calcination temperature / °C	TS-1 Crystallinity / %	Pd particle size / nm <sup>[a]</sup>	Au particle size / nm <sup>[a]</sup>	Pt particle size / nm <sup>[a]</sup>	BET surface area / m <sup>2</sup> g <sup>-1</sup> <sup>[b]</sup>
TS-1	Uncalcined	100	-	-	-	
5 wt. % Pd/ TS-1	400	85.6	15.2	-	-	340
	800	59.7	66.0	-	-	310
2.5 wt. % Au – 2.5 wt. % Pd/ TS-1	400	83.0	-	17	-	302
	800	56.3	17	32	-	292
2 wt. % Au – 2 wt. % Pd – 1 wt. % Pt/ TS-1	400	68.0	-	46.7	-	299
	800	33.8	-	50.3	28.7	280

<sup>[a]</sup> Determined using the Scherrer equation, <sup>[b]</sup> Determined via N<sub>2</sub> physisorption.

Using the principle reflections associated with TS-1 ( $\theta = 23.1^\circ$ ,  $24.4^\circ$  and  $24.5^\circ$ ) it is possible to determine that impregnation of TS-1 with Pd, followed by calcination at 400 °C leads to a 14.6 % decrease in crystallinity of TS-1 with metal impregnation and heat treatment. By increasing the calcination temperature to 800 °C the crystallinity of the TS-1 decreases further, reaching 59.7 %. Across the same temperature range the BET surface area of the 5 wt. % Pd / TS-1 catalyst falls from 340 to 310 m<sup>2</sup>g<sup>-1</sup>. The observed decrease in catalyst activity towards the ammoxidation of cyclohexanone may partly be attributed to a structural change in the TS-1 support. However it has already been shown in Chapter 4 that comparable rates of cyclohexanone conversion and oxime selectivity are observed for both the bare and metal loaded TS-1 (calcined, static air, 3 h, 400 °C), when *ex-situ* H<sub>2</sub>O<sub>2</sub> is utilised, so the decrease in catalytic activity may not be solely attributed to this loss in crystallinity.

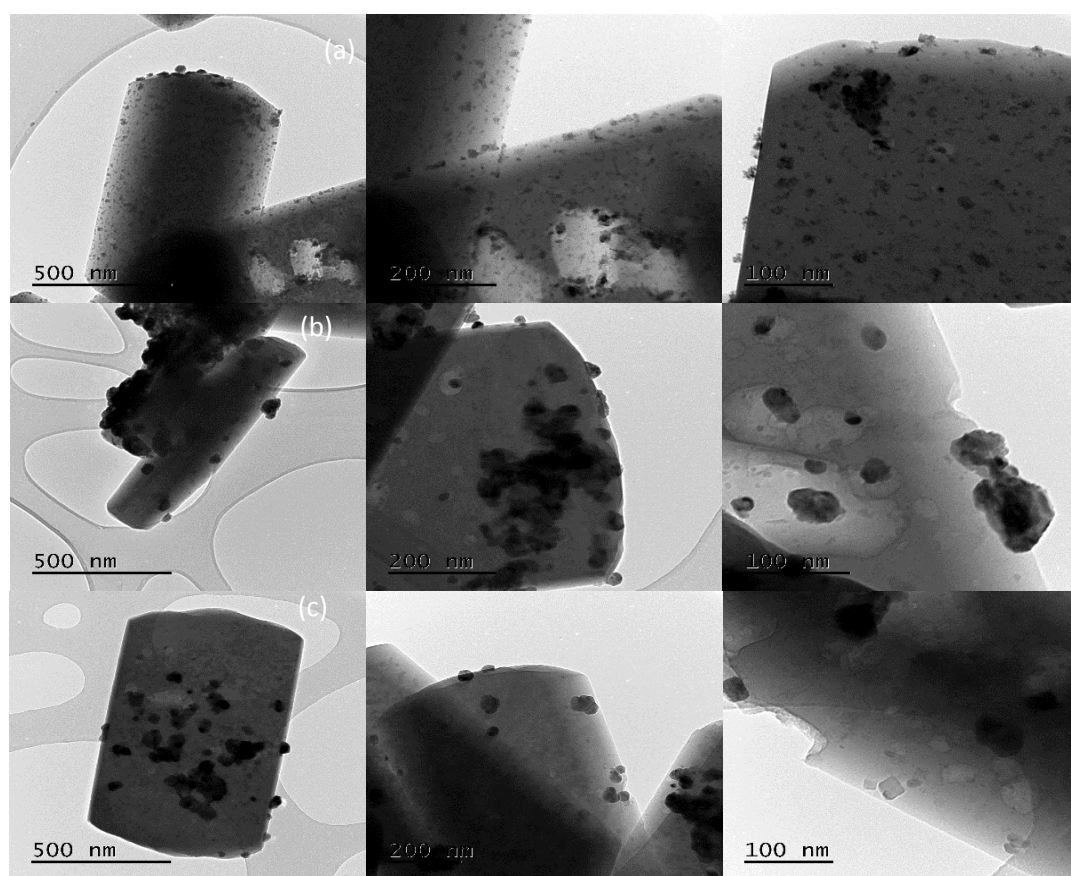
To determine the effect of increasing calcination temperature upon the active phase, responsible for H<sub>2</sub>O<sub>2</sub> synthesis, the Pd nanoparticle size was determined using the PdO reflection at  $35^\circ$  (Appendix 5.1 Figure A1). As shown in Table 5.2, upon increasing the calcination temperature from 400 °C to 800 °C, the calculated PdO nanoparticle size increases from 15.2 to 66 nm. However it should be noted that the detection limit of XRD is

approximately 5 nm and as such it would not be possible to observe Pd nanoparticles below this limit. Investigation of Pd nanoparticle size by XRD is therefore qualitative only.

Further investigation, by XPS is shown in Appendix 5.3 Table A1. It is observed Pd is present as  $\text{Pd}^{2+}$ , which agrees with the observation of PdO in the XRD analysis. It can further be observed that as calcination temperature increases, the dispersion of Pd on the support decreases, with atomic concentration of Pd decreasing from 1.14 % at a calcination temperature of 400 °C to 1.01 % at 800 °C, this correlates with analysis by XRD, which shows increasing peak intensity of the Pd reflection at 35° and CO chemisorption which shows decrease dispersion of Pd on the support.

It can also be seen that as calcination temperature rises the Si : Ti ratio decreases, from 103.9 at 400 °C to 79.7 when calcined at 800 °C. This suggests that at elevated temperatures the concentration of Ti at the surface increases, which again correlates with the loss of crystallinity from analysis.

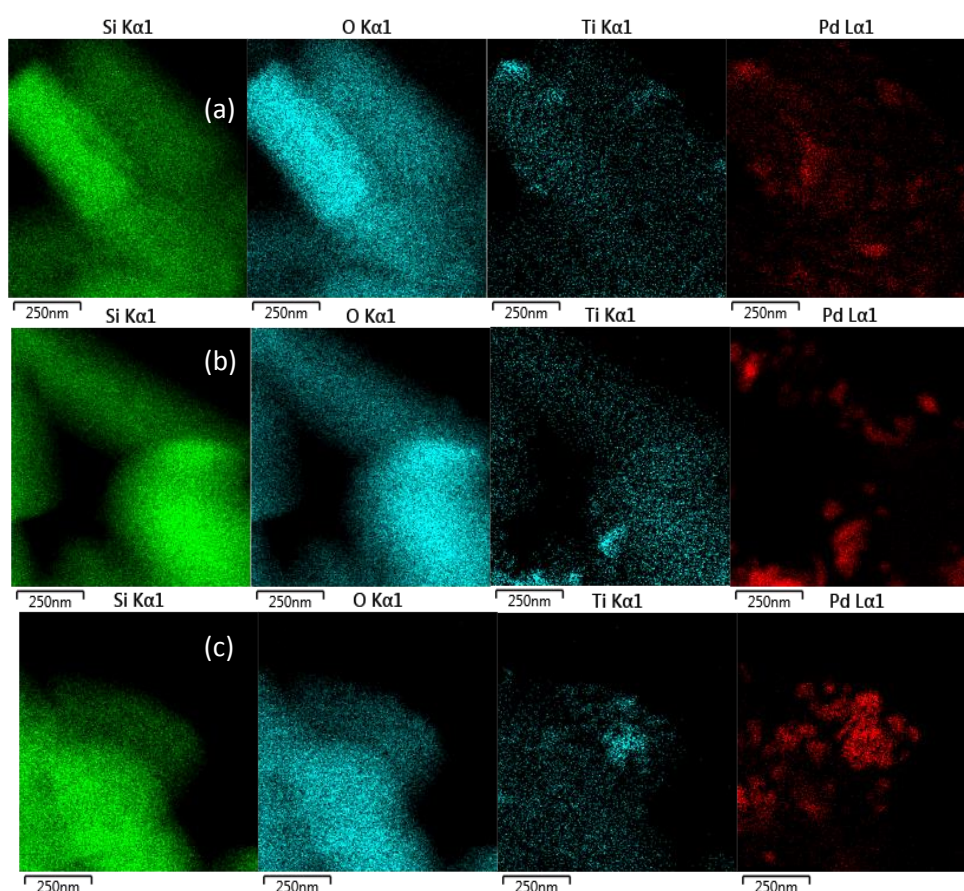
Analysis of the 5 wt. % Pd / TS-1 catalysts exposed to increasing calcination temperature by Transmission Electron Microscopy (TEM) can be seen in Figure 5.4



**Figure 5.4.** Transmission Electron Microscopy of 5 wt. % Pd / TS-1 exposed to calcination temperatures of <sup>(a)</sup> 400 °C, <sup>(b)</sup> 600 °C, <sup>(c)</sup> 800 °C (3 h, 20 °C min<sup>-1</sup>, static air).



It can be observed from Figure 5.4, that metal nanoparticle size increases dramatically with increasing calcination temperature, however particle size distribution could not be carried out due to particle boundary deformation. As nanoparticles agglomerate, with increasing calcination temperature, it is not possible to differentiate one nanoparticle from its neighbours. However, it is clear to see from Figure 5.4 that as calcination temperature increases the nanoparticles agglomerate. This is in agreement with investigation by CO chemisorption (Table 5.1), XPS (Appendix 1.3 and XRD (Table 5.2). In addition to this investigation by STEM – EDX, Figure 5.5, reveals that Pd nanoparticles becomes less disperse with increasing calcination temperature.

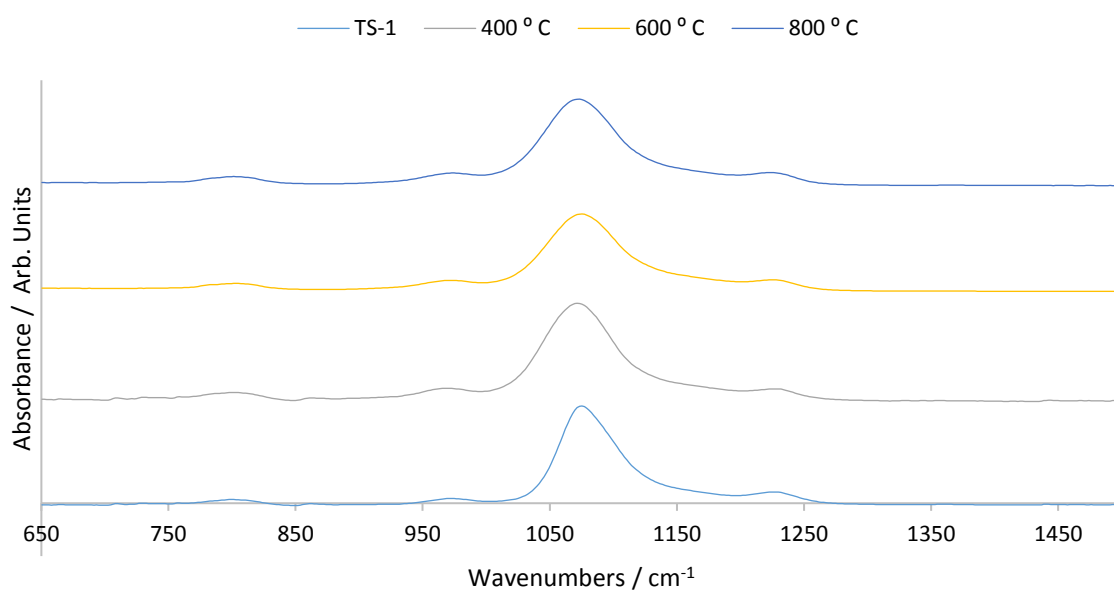


**Figure 5.5.** STEM – EDX analysis of 5 wt. % Pd / TS-1 exposed to calcination temperatures of (a) 400 °C, (b) 600 °C, (c) 800 °C (3 h, 20 °C min<sup>-1</sup>, static air). Si (Green), O (Blue), Ti (Blue), Pd (Red).

The increase in Pd nanoparticle size may contribute to the observed decrease in catalyst activity for both H<sub>2</sub>O<sub>2</sub> synthesis and cyclohexanone ammoximation reactions. It is suggested that ‘small’ nanoparticles (those below 5nm in diameter), are highly active for the synthesis of H<sub>2</sub>O<sub>2</sub> while larger nanoparticles are less active. By increasing the calcination temperature, the Pd particle size increases and in turn catalyst activity for H<sub>2</sub>O<sub>2</sub> synthesis decreases.

These two factors; the loss in TS-1 crystallinity and Pd nanoparticle growth may both lead to lower rates of cyclohexanone oxime formation by (a) decreasing the rate of  $\text{H}_2\text{O}_2$  synthesis through Pd particle growth and (b) lowering the rate of  $\text{H}_2\text{O}_2$  activation on the TS-1 support through loss of framework Ti (IV) sites. Both of these would decrease the rate of hydroxylamine formation and the subsequent synthesis of cyclohexanone oxime.

Finally investigation of the 5 wt. % Pd / TS-1 catalysts exposed to increasing calcination temperature (400 – 800 °C) by FTIR can be seen in Figure 5.6.



**Figure 5.6.** FTIR spectra of 5 wt. % Pd / TS-1 catalysts calcined at 400 – 800 °C (3 h, static air, 20 °C min<sup>-1</sup>)

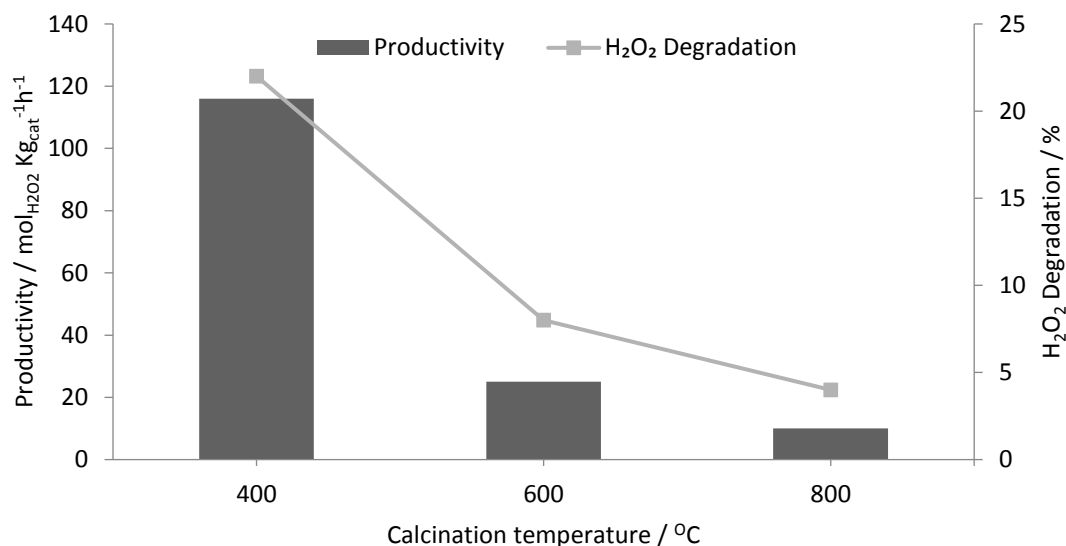
It can be observed that no discernible change can be observed in the structure of TS-1, upon impregnation of Pd and subsequent calcination at increasing temperatures when investigated by FTIR. It is possible to observe four distinct infrared bands in Figure 5.6 at 800 cm<sup>-1</sup> and 1100 cm<sup>-1</sup> assigned to lattice modes associated with internal linkages in tetrahedral  $\text{SiO}_4$ , at 990 cm<sup>-1</sup> assigned to stretching vibrations of  $\text{SiO}_4$  tetrahedra bound to Ti atoms as Si-O-Ti linkages and at 1240 cm<sup>-1</sup> assigned to tetrahedral Ti present in the TS-1 framework.

The activities of 5 wt. % Pd / TS-1 catalysts for  $\text{H}_2\text{O}_2$  synthesis following calcination at 400, 600 and 800 °C are shown in Figure 5.7. These studies were carried out using standard  $\text{H}_2\text{O}_2$  synthesis and degradation procedures, as outlined in Section 5.1.

It was shown in Figure 5.3 that as the calcination temperature increases activity towards cyclohexanone ammoxidation decreases. Based upon the data in Figure 5.4 it is possible to

conclude that this is due to a decrease in productivity for  $\text{H}_2\text{O}_2$  synthesis at elevated calcination temperatures.

Figure 5.7 shows the effect of calcination temperature on the catalytic activity of 5 wt. % Pd towards the direct synthesis of  $\text{H}_2\text{O}_2$  and its subsequent degradation.



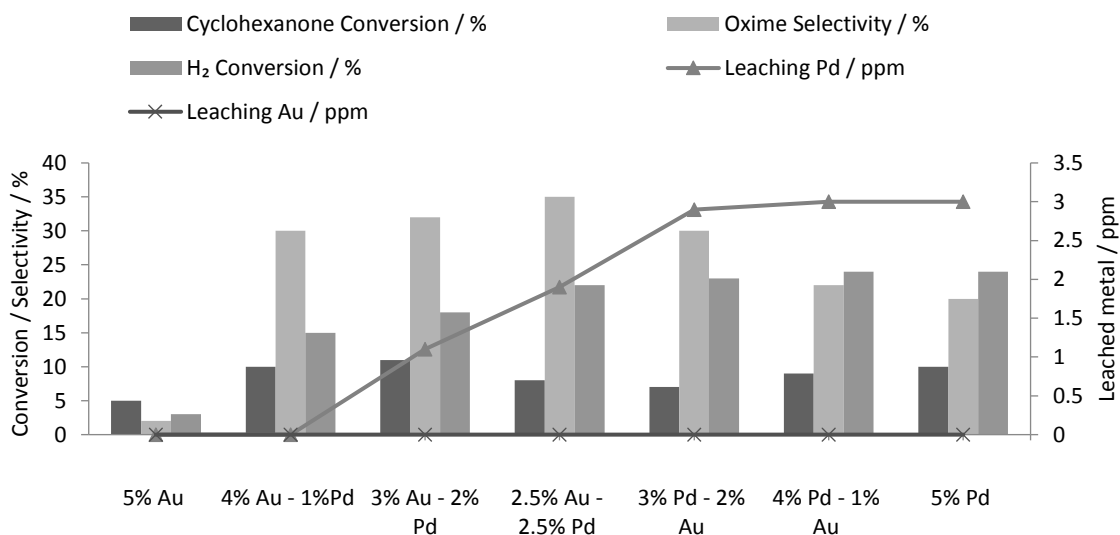
**Figure 5.7.** The effect of calcination temperature on the activity of 5 wt. % Pd / TS-1 towards the direct synthesis and degradation of  $\text{H}_2\text{O}_2$ .

**Reaction conditions:** 5 wt. % Pd / TS-1 (0.01 g), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 5.6 g MeOH + 2.9 g  $\text{H}_2\text{O}$  (66 wt. % MeOH), 2 °C.

It is observed in, Figure 5.7, that catalytic activity for  $\text{H}_2\text{O}_2$  synthesis decreases substantially with increasing calcination temperature, from 116 to 10  $\text{mol}_{\text{H}_2\text{O}_2} \text{Kg}_{\text{cat}}^{-1} \text{h}^{-1}$  for calcinations at 400 °C and 800 °C respectively (a percentage loss of approx. 90 %). As with the ammoximation of cyclohexanone, catalytic activity towards the synthesis of  $\text{H}_2\text{O}_2$ , also decreases with increasing calcination temperature, to a minimum of 6 % when a calcination temperature of 800 °C is employed. This can be attributed to an increase in size of Pd particles with increasing temperature, as shown via XRD (Table 5.2) and TEM analyses (Figure 5.4).

### 5.2.3. The effect of Au-Pd metal ratio on the ammoximation of cyclohexanone to cyclohexanone oxime via direct synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub>

It has been shown that bi-metallic Au-Pd/ TS-1 catalysts are active for the direct synthesis of H<sub>2</sub>O<sub>2</sub> in a H<sub>2</sub>O / MeOH system, at both 2 °C and elevated temperatures (Chapter 4 Section 4.2.1). It has furthermore been demonstrated (Chapter 4 Section 4.2.4) that these catalysts are active for the ammoximation of cyclohexanone via the addition of H<sub>2</sub>O<sub>2</sub> and that when compared to TS-1 alone there is little difference in either selectivity towards the oxime or cyclohexanone conversion. Mono- and bi-metallic Au – Pd / TS-1 catalysts (of varying Au: Pd ratio) were investigated for the ammoximation of cyclohexanone with H<sub>2</sub>O<sub>2</sub> synthesised *in situ* and the results of these studies are shown in Figure 5.8.



**Figure 5.8.** The effect of Au : Pd ratio on the ammoximation of cyclohexanone. Total metal loading on TS-1 is 5 wt. %.

**Reaction conditions:** Catalyst (0.05 g), cyclohexanone (0.13 g, 1.3 mmol), NH<sub>3</sub> (28 wt. %, 0.08g, 1.3mmol), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g H<sub>2</sub>O (66 wt. % t-BuOH), 80 °C.

It is observed, Figure 5.8, that bimetallic Au-Pd catalysts show consistently low cyclohexanone conversion of 5 – 11% under the reaction conditions used. However the introduction of Pd to a Au-only catalyst improves oxime selectivity dramatically, from 2 % for 5 wt. % Au / TS-1 to 30% for 4 wt. % Au - 1 wt. % Pd / TS-1. Selectivity towards cyclohexanone oxime follows a volcano-like trend that correlates with Pd content until Au : Pd ratio of 1:1 is reached, where selectivity towards the oxime is seen to be 35 %. This is particularly interesting as the mono-metallic Au catalyst shows very little activity towards the ammoximation of cyclohexanone and this can be related to its low activity towards the direct synthesis of H<sub>2</sub>O<sub>2</sub>, as shown in Figure 5.9. However by incorporating Au into a Pd

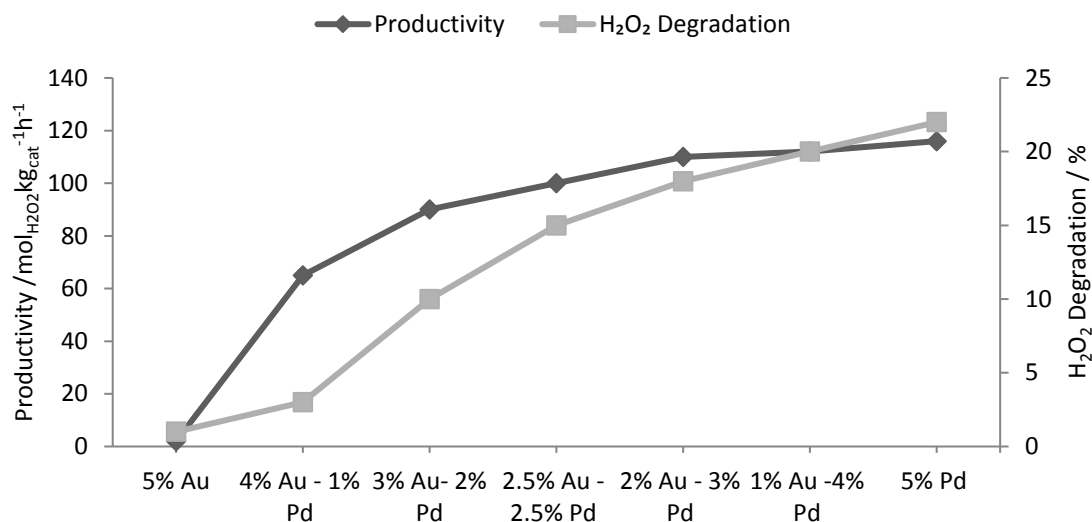
catalyst so that the ratio of the two metals is 1 : 1 by wt. % it is possible to dramatically improve the selectivity towards cyclohexanone oxime. Beyond a 1:1 ratio of Au: Pd, further increasing the Pd content leads to a decrease in oxime selectivity.

H<sub>2</sub> conversion is also observed to increase with Pd content, reaching a maximum at a Au: Pd ratio of 1:1. Beyond this point H<sub>2</sub> conversion remains fairly constant. This correlates with H<sub>2</sub>O<sub>2</sub> synthesis rates over the same catalyst series, which do not differ greatly. Indeed, 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 and 5 wt. % Pd / TS-1 show comparable H<sub>2</sub>O<sub>2</sub> productivities, at 100 and 116 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> respectively, as seen in Figure 5.9.

It is known that upon calcination, Au-Pd particles on a range of oxide supports form a core-shell morphology consisting of a Au-rich core surrounded by a PdO shell<sup>5</sup>. These bi-metallic systems show superior activity and selectivity towards H<sub>2</sub>O<sub>2</sub> when compared to monometallic counterparts and enhancement in the activity of Au-Pd oxide supported catalysts towards H<sub>2</sub>O<sub>2</sub> synthesis has been attributed to electronic modification of the metals<sup>6</sup>. In these studies particle size has been related to the Au: Pd ratio, with smaller particles containing higher concentrations of Pd. It is possible that upon calcination of the bi-metallic TS-1 supported catalysts a degree of alloying is induced and this may explain the enhancement in selectivity towards the oxime observed for bimetallic catalysts in Figure 5.8. It is suggested that further investigation in to the morphology of the metal nanoparticles is required to determine the extent of alloying between Au and Pd and to determine if a core shell morphology is adopted as it is on oxide supports, such as P25 TiO<sub>2</sub>.

Leaching studies reveal no loss of Au regardless of total content. In contrast Pd leaching increases with the total Pd loading, to a maximum of 3 ppm for the 5 wt. % Pd / TS-1 catalyst which is consistent with trends observed in Figure 5.1.

Investigation of these Au-Pd catalysts supported on TS-1 for the direct synthesis and degradation of H<sub>2</sub>O<sub>2</sub> is shown in Figure 5.9.



**Figure 5.9.** The effect of the Au : Pd ratio on the direct synthesis and degradation of H<sub>2</sub>O<sub>2</sub>. Total metal loading on TS-1 is 5 wt. %. **Reaction conditions:** Catalyst (0.01 g), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g MeOH + 2.9g H<sub>2</sub>O (66 wt. % MeOH), 2 °C.

It is observed in Figure 5.9 that catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis is correlated to Pd content, with the rate of H<sub>2</sub>O<sub>2</sub> synthesis increasing with Pd content. Catalytic activity towards the synthesis of H<sub>2</sub>O<sub>2</sub> increases from 2 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> for 5 wt. % Au / TS-1 to 116 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> for 5 wt. % Pd / TS-1. Unlike the ammoximation of cyclohexanone, activity towards H<sub>2</sub>O<sub>2</sub> synthesis does not show a volcano-like trend.

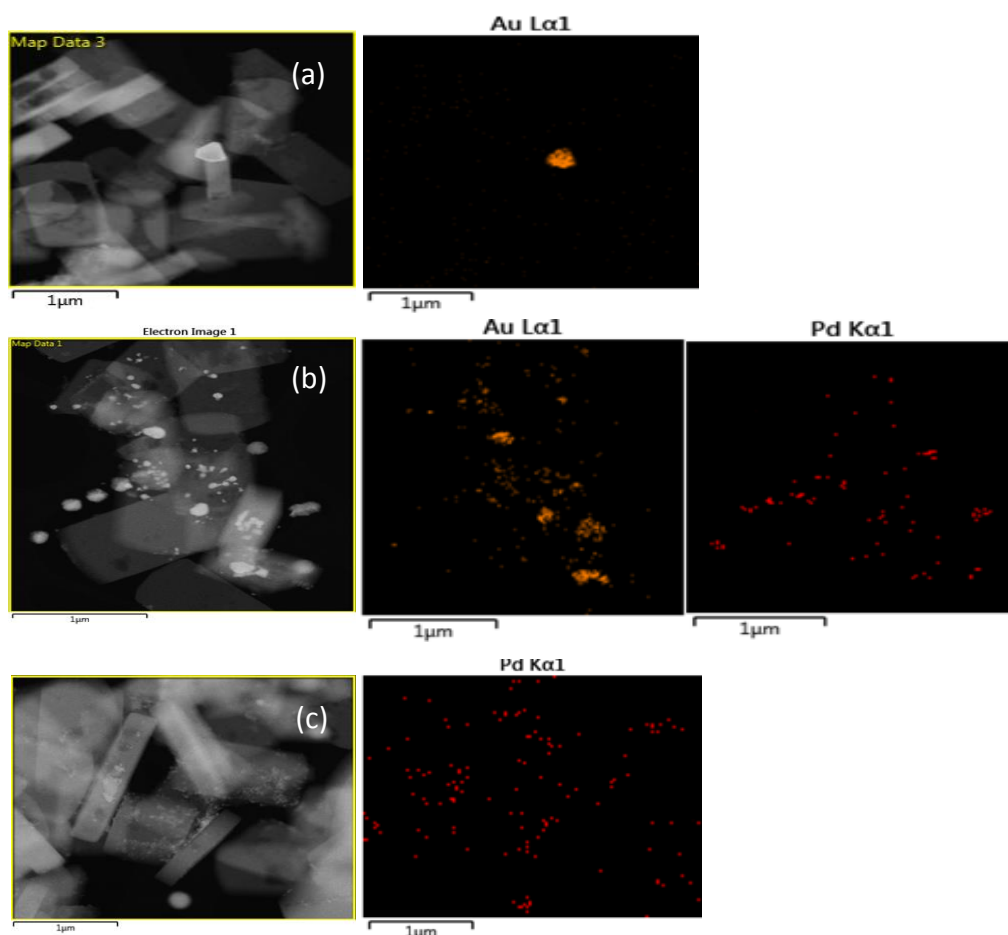
It is suggested that at higher Pd content the rate of H<sub>2</sub>O<sub>2</sub> synthesis exceeds that of hydroxylamine formation by the Ti (IV) active sites within the TS-1 support's pores and as such degradation of H<sub>2</sub>O<sub>2</sub> formed but not involved in hydroxylamine synthesis increases. This degradation may either be catalytic or as a result of the reaction conditions utilised. As Au is shown to have limited activity towards the ammoximation of cyclohexanone and no improvement in activity towards H<sub>2</sub>O<sub>2</sub> synthesis is observed when both Pd and Au are incorporated onto the same support it may be that the role of Au, when incorporated into a Pd / TS-1 catalyst is to limit the rate of H<sub>2</sub>O<sub>2</sub> synthesis. By ensuring the rate of H<sub>2</sub>O<sub>2</sub> synthesis does not exceed the rate of hydroxylamine formation it is possible to ensure greater oxime selectivity.

It is suggested that catalyst design to ensure the rate of H<sub>2</sub>O<sub>2</sub> synthesis is equal to the rate of hydroxylamine formation is key in producing a highly selective catalyst.

Investigation of these bi-metallic Au – Pd / TS-1 catalysts by XRD shows an increase in the intensity of the reflections associated with Au metal nanoparticles at 38 ° (Appendix 5.1, Figure A4) with increasing Au loading, suggesting the presence of Au nanoparticles of larger

than 5 nm. No peaks that can be attributed to Pd species are observed, regardless of Pd loading, which suggests that the particle size of the Pd nanoparticles is below the detection limit of this technique, approximately 5nm.

Au-Pd catalysts prepared using a variety of oxide supports such as P25 TiO<sub>2</sub> are reported to show the greatest activity towards H<sub>2</sub>O<sub>2</sub> synthesis at a Au : Pd ratio of 1: 1. As such a 2.5 wt. % Au - 2.5 wt. % Pd catalyst would be expected to show a higher rate of H<sub>2</sub>O<sub>2</sub> synthesis than monometallic 5 wt. % Pd or 5 wt. % Au catalysts <sup>6,7</sup> following calcination in static air, catalysts comprising of Au-Pd impregnated on certain oxide supports, such as P25 TiO<sub>2</sub>, present alloyed nanoparticles core-shell morphology, where the core is Au-rich and the shell Pd-rich. Investigation of the Au-Pd catalysts used in Figure 5.7 by STEM- EDX mapping of Au and Pd or regions within the same catalysts shown in Figure 5.10.



**Figure 5.10** STEM-EDX mapping of regions in (a) 5 wt. % Au/ TS-1, (b) 2.5 wt. % Au - 2.5 wt. % Pd / TS-1 and (c) 5 wt. % Pd/ TS-1

STEM-EDX, shown in in Figure 5.10 show the presence of large, poorly dispersed Au particles for 5 wt. % Au/ TS-1 (a). This is in agreement with XRD data in Table 5.2. Meanwhile the

mono-metallic Pd catalyst (5 wt. % Pd/ TS-1, (c)) is observed to contain much smaller metal nanoparticles that are highly dispersed, again in agreement with XRD data, where no characteristic PdO peaks are observed (Appendix 5.1, Figure A1). The combination of both Au and Pd onto the same support (b) is shown to improve the dispersion of Au. This is found to be consistent with previous reports by Hutchings and co-workers<sup>8</sup>. Following metal impregnation and calcination, there is some loss in total surface area (Table 5.2), from 340 m<sup>2</sup>g<sup>-1</sup> for unmodified TS-1 to a minimum of 302 m<sup>2</sup>g<sup>-1</sup> for 2.5 wt. % Au – 2.5 wt. % Pd / TS-1. This loss in surface area is not deemed significant to overall catalytic activity. It was shown in Chapter 4 (Section 4.2.4) that there is very little difference in activity of the mono- and bi-metallic Au-Pd catalysts towards the ammoximation of cyclohexanone via the addition of preformed H<sub>2</sub>O<sub>2</sub> and so the slight loss in total surface area, possibly through the blocking of pores by metal incorporation, does not adversely affect the activity of TS-1.

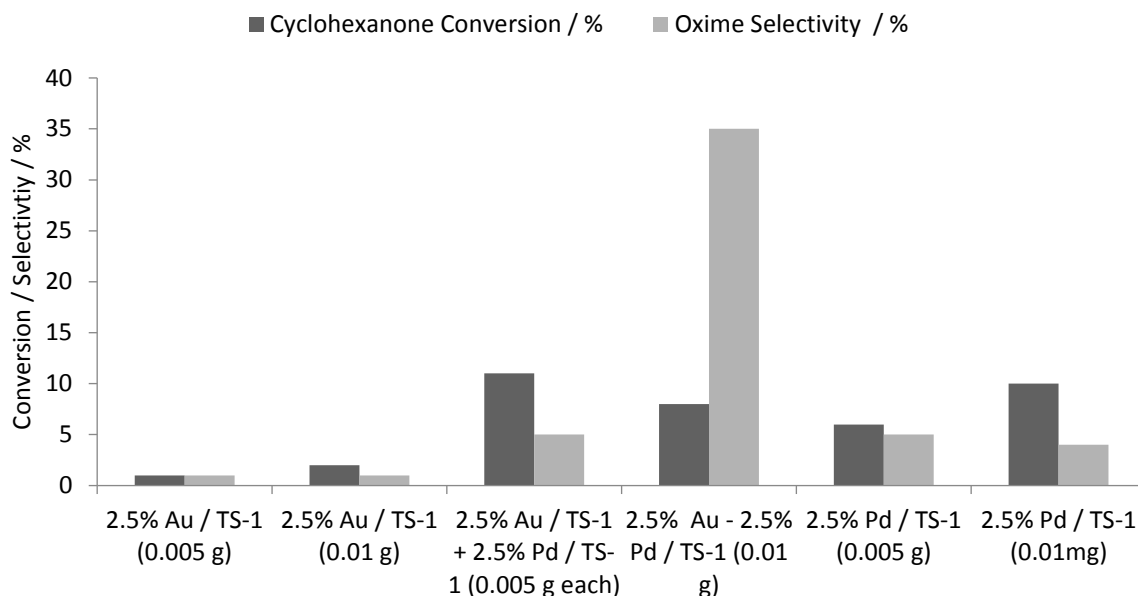
It has previously been reported by Hutchings and co-workers that the alloying of Au and Pd on a range of oxide supports results in electronic modification of the Pd, producing a more selective catalyst <sup>6</sup>. A lack of complete alloying between Au and Pd, when supported on TS-1, may be responsible for the correlation between Pd loading and increased H<sub>2</sub>O<sub>2</sub> synthesis and degradation rates.

#### 5.2.4. Investigating the role of Au in improving catalytic selectivity towards cyclohexanone oxime.

As previously shown in Figure 5.8 addition of Pd to a Au/ TS-1 increases cyclohexanone oxime selectivity. Contrasting this, the activity towards the direct synthesis and subsequent degradation of H<sub>2</sub>O<sub>2</sub> increases as the catalyst becomes more Pd-rich (Figure 5.9).

It is well known that upon calcination, Au-Pd alloyed nanoparticles can form on a variety of oxide supports as well as carbon and the resulting catalysts have been reported to offer improved activity towards H<sub>2</sub>O<sub>2</sub> synthesis compared to the mono-metallic analogues<sup>9</sup>. To investigate whether such a synergistic effect is in operation for bimetallic Au-Pd/ TS-1 catalysts during cyclohexanone ammoximation, the selectivity and conversion observed over bi-metallic 2.5 wt. % Au- 2.5 wt. % Pd / TS-1 were compared to those observed when monometallic 2.5 wt. % Au / TS-1 and 2.5 wt. % Pd / TS-1 were used separately and in combination as a physical mixture. The results are shown in Figure 5.11.





**Figure 5.11** Effect of combining Au and Pd on the same support and as a physical mixture towards the ammoxidation of cyclohexanone.

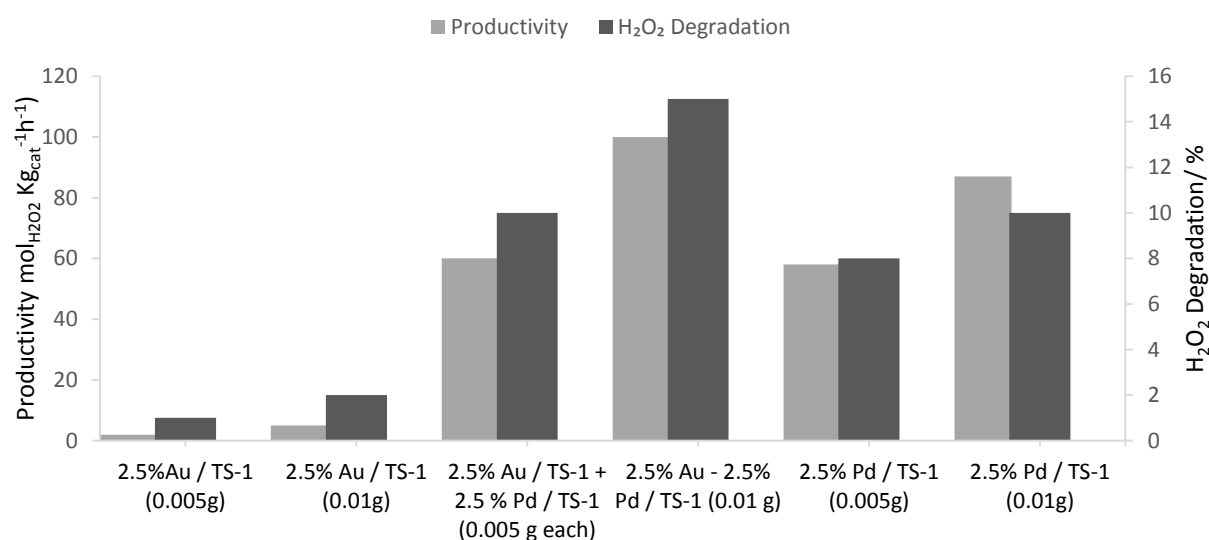
**Reaction conditions:** Catalyst, cyclohexanone (0.13 g, 1.3 mmol),  $\text{NH}_3$  (0.08g, 28 wt. %, 1.3 mmol), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g  $\text{H}_2\text{O}$  (66 wt. % t-BuOH), 80 °C.

Figure 5.11 demonstrates the beneficial effect of co-impregnating Au and Pd onto the same TS-1 support. As shown in Figure 5.8 it is only when both Au and Pd are incorporated onto the TS-1 support that an improvement in selectivity is observed. As in Figure 5.8 monometallic Au catalysts show poor cyclohexanone conversion and selectivity towards the oxime when compared to analogous Pd- only catalysts. This is again observed when comparing 2.5 wt. % Au / TS-1 and 2.5 wt. % Pd / TS-1, with the Pd-only catalyst showing 5 times the rate of cyclohexanone conversion when compared with the Au-only analogue (10 % and 2 % respectively). When physical mixtures of the two catalysts are assessed (0.005 g of each catalyst) conversion rates and selectivity towards the oxime are comparable to those observed for the Pd-only catalyst, which is consistent with the low cyclohexanone conversion rate observed for 5 wt. % Au / TS-1 in Figure 5.8.

When a bi-metallic 2.5 wt. % Au - wt. 2.5% Pd / TS-1 catalyst is investigated a dramatic increase in selectivity towards the oxime is observed, from 5% when a physical mixture of the two catalysts is utilised to 35% for the bi-metallic catalyst. The improvement in catalytic selectivity towards the oxime may be attributed to the formation of Au-Pd nanoparticles on the surface of the TS-1 support. The formation of these Au-Pd bi-metallic nanoparticles on various oxide supports has previously been shown to lead to improved catalytic activity for the direct synthesis of  $\text{H}_2\text{O}_2$  in comparison to the monometallic catalysts<sup>9</sup>. The effect of

combining both metals on the same support for the direct synthesis of  $\text{H}_2\text{O}_2$  is discussed later. As the rate of  $\text{H}_2\text{O}_2$  synthesis is increased the concentration of  $\text{H}_2\text{O}_2$  available to be activated by the Ti (IV) sites present in TS-1 increases. This leads to an increase in the concentration of Ti-OOH sites, thereby increasing the rate of hydroxylamine formation and thus oxime formation. It may therefore be that the incorporation of both metals on to the same support is key in producing a catalyst where the rate of  $\text{H}_2\text{O}_2$  synthesis is closer to the rate of hydroxylamine formation. This would result in greater oxime selectivity based on  $\text{H}_2$ . That is more  $\text{H}_2$  is utilised in the formation of cyclohexanone oxime, rather than in the formation of  $\text{H}_2\text{O}$ , via the degradation of  $\text{H}_2\text{O}_2$ , or unwanted by-products such as cyclohexanol. Further work is needed to determine whether optimisation of the rates of  $\text{H}_2\text{O}_2$  and hydroxylamine synthesis is a key factor in further enhancing catalyst selectivity. It has been demonstrated previously in Figure 5.8 that the addition of Au to a Pd / TS-1 catalyst improves selectivity towards cyclohexanone oxime at comparable cyclohexanone conversion.

Figure 5.12 shows the improvement in the rate of  $\text{H}_2\text{O}_2$  synthesis, observed when Au and Pd are co-impregnated onto the same support.



**Figure 5.12.** Effect of combining Au and Pd on the same support towards the direct synthesis and degradation of  $\text{H}_2\text{O}_2$ .

**Reaction conditions:** 5 wt. % Pd / TS-1 (0.01 g), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 5.6 g MeOH + 2.9 g  $\text{H}_2\text{O}$  (66 wt. % MeOH), 2 °C.

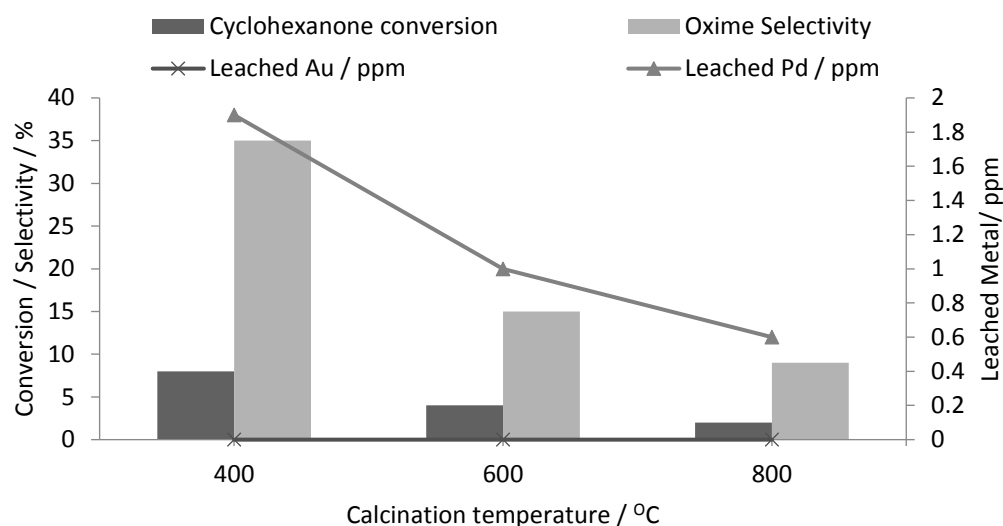
Figure 5.12 shows a similar trend for  $\text{H}_2\text{O}_2$  synthesis as that observed in Figure 5.11 for the ammoxidation of cyclohexanone. Indeed, a catalyst prepared by co impregnation of Au and Pd onto the TS-1 support shows a higher  $\text{H}_2\text{O}_2$  synthesis rate than the analogous physical

mixture of monometallic catalysts (100 and 60 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> respectively). It is clear from Figure 5.11 that the monometallic 2.5 wt. % Pd/ TS-1 catalyst is far more active for the direct synthesis of H<sub>2</sub>O<sub>2</sub> than the analogous Au-only catalyst and that a physical mixture of the two mono-metallic catalysts offers H<sub>2</sub>O<sub>2</sub> synthesis rates comparable to the sum of the two catalysts. Impregnation of Au and Pd onto the same support produces a catalyst that shows significantly higher activity for H<sub>2</sub>O<sub>2</sub> synthesis than a physical mixture of the two monometallic catalysts. This suggests that the incorporation of the two metals is key for H<sub>2</sub>O<sub>2</sub> synthesis, as reported previously by Hutchings and co-workers<sup>10</sup>. It has been suggested that the alloying of these two metals results in electronic modification of the Pd and that this results in the formation of a more active H<sub>2</sub>O<sub>2</sub> synthesis catalyst<sup>11</sup>.

#### 5.2.5. The effect of calcination temperature on 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 activity towards the ammoxidation of cyclohexanone.

It has previously been shown for 5 wt. % Pd / TS-1 catalyst, that catalytic activity for both cyclohexanone ammoxidation and direct H<sub>2</sub>O<sub>2</sub> synthesis decreases as the calcination temperature increases. However stability of the catalyst, in the ammoxidation reaction, improves.

Comparison of 5 wt. % Pd/ TS-1 and 2.5 wt. % Au-2.5 wt. % Pd / TS-1 (both calcined at 400 °C, 3 h, static air, 20 °C min<sup>-1</sup>) has shown that the bi-metallic Au-Pd catalyst shows higher catalytic activity towards cyclohexanone ammoxidation than the monometallic Pd catalyst. The effect of varying the calcination temperature on the catalytic performance of 2.5 wt. % Au - 2.5 wt. % Pd / TS-1 catalyst was investigated to determine if the deleterious effect of a high calcination temperature, observed for the Pd mono-metallic, can be offset through the incorporation of Au. The results of this study are shown in Figure 5.13.

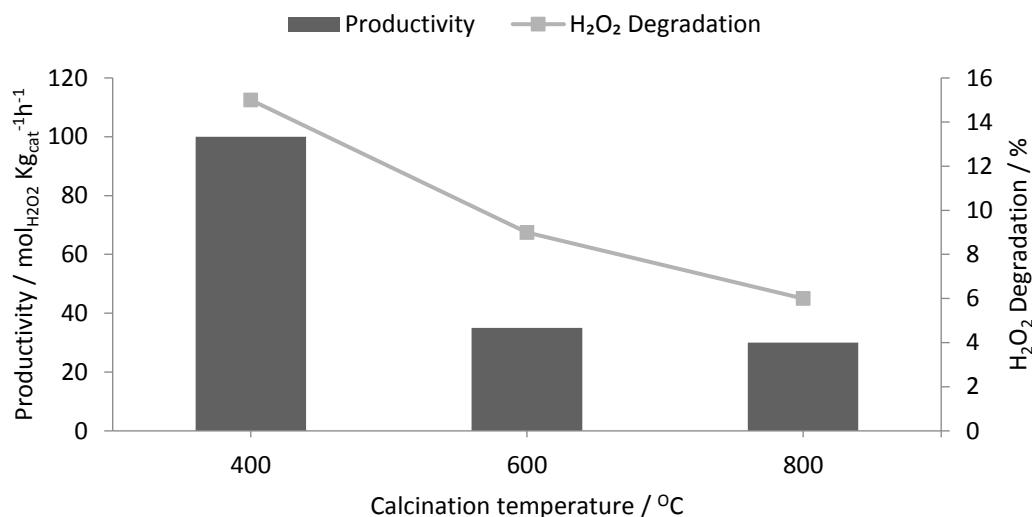


**Figure 5.13.** Effect of calcination temperature on the catalytic performance of 2.5 wt. % Au- 2.5 wt. % Pd/ TS-1 for cyclohexanone ammoximation.

**Reaction conditions:** Catalyst (0.05 g), cyclohexanone (0.13 g, 0.13 mmol),  $\text{NH}_3$  (0.08g, 28 wt. %, 1.3 mmol), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g  $\text{H}_2\text{O}$  (66 wt. % t-BuOH), 80 °C.

It is observed that, as with the 5 wt. % Pd / TS-1 catalyst, the calcination temperature increases there is a substantial decrease in catalyst activity, with both cyclohexanone conversion and oxime selectivity decreasing, from 8 and 35 % when calcined at 400 °C to 2 and 9 % when the catalyst is calcined at 800 °C. Unlike the mono-metallic Pd catalyst, some activity is retained following calcination at 800 °C. In a similar manner to the Pd only catalyst a decrease in leached Pd is observed as calcination temperature increases. Interestingly, no leached Au is observed regardless of calcination temperature. Some activity towards the ammoximation of cyclohexanone is retained suggesting that the introduction of Au into a Pd-only catalyst is able to off-set the deleterious effects of increased calcination temperature on catalyst activity towards the ammoximation of cyclohexanone.

Figure 5.14 shows the effect of calcination temperature on the direct synthesis and degradation of  $\text{H}_2\text{O}_2$  by 2.5 wt. % Au – 2.5 wt. % Pd / TS-1.



**Figure 5.14.** Effect of calcination temperature on the catalytic activity of 2.5 wt. % Au-2.5 wt. % Pd / TS-1 for the direct synthesis and degradation of H<sub>2</sub>O<sub>2</sub>.

**Reaction conditions:** 2.5 wt.% Au- 2.5 wt. % Pd / TS-1 (0.01 g), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> =0.525, 1200 rpm, 30 min, 5.6 g MeOH + 2.9 g H<sub>2</sub>O (66 wt. % MeOH), 2 °C.

It is observed that, as with 5 wt. % Pd / TS-1 (Section 5.2.2), increasing the calcination temperature causes a decrease in the activity of the catalyst for direct H<sub>2</sub>O<sub>2</sub> synthesis. Indeed, when calcined at 400 °C the rate of H<sub>2</sub>O<sub>2</sub> synthesis is 100 mol<sub>H2O2</sub>Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>, whilst by increasing the calcination temperature to 800 °C productivity decreases to 30 mol<sub>H2O2</sub>Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>. Further investigation has shown that catalytic activity towards the degradation of H<sub>2</sub>O<sub>2</sub> also decreases with calcination temperature. This is attributed to the development of larger metal nanoparticles, as confirmed by XRD analysis (Table 5.2). In particular the increased intensity of peaks at 2θ values characteristic of Au (38° and 45°)(Appendix 5.1, Figure A2) suggests growth of Au particles with increasing calcination temperature.

Table 5.2 shows that as the calcination temperature increases the crystallinity of TS-1 decreases. Upon calcination at 400 °C crystallinity decreases to 83 % and this further decreases to 56.3 % upon calcination at 800 °C. This loss in crystallinity follows a similar trend to that observed for 5 wt. % Pd / TS-1, discussed in Section 5.2.2. Further investigation by XRD (Table 5.2), shows that a contrast with the monometallic Pd / TS-1 catalyst, no Pd reflections are observed for the bimetallic 2.5 wt. % Au – 2.5 wt.% Pd/ TS-1 catalyst (Appendix 5.1, Figure A2) following calcination at 400 °C. However, increasing the calcination temperature to 600 and 800 °C leads to clear reflections associated with PdO (34°). Indeed, the average Pd nanoparticle size determined using the Scherrer equation was 17 nm, when a calcination temperature of 800 °C was utilised. This is much lower than that observed when 5 wt. % Pd / TS-1 was calcined at 800 °C (Table 5.2), and may be the reason why the 2.5 wt.

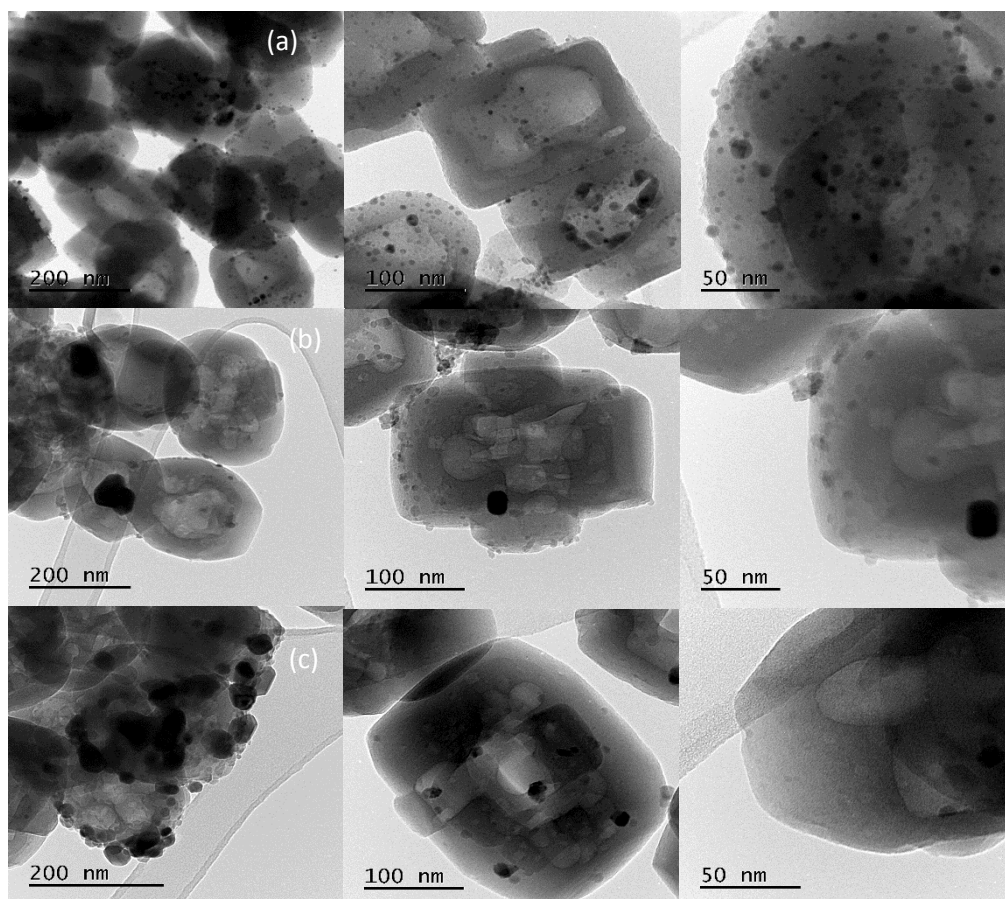
% Au – 2.5% wt. Pd / TS-1 catalyst retains a degree of activity following calcination at 800 °C, as shown in Figure 5.12. The development of XRD reflections associated with PdO with increasing temperature correlates well with analysis by XPS (Appendix 5.3, Table A.2). It is seen that the atomic concentration of Pd decreases with increasing temperature, from 0.4 to 0.13 %, suggesting a decrease in the dispersion of Pd on the support.

Unlike Pd, XRD analysis of bimetallic Au – Pd/ TS-1 shows reflections associated with Au (38°, 44° and 70°) regardless of calcination temperature, suggesting Au is present as larger, poorly dispersed, nanoparticles even when calcined at 400 °C.

Further investigation by XPS shows that the Pd : Au ratio decreases drastically with temperature from a Pd : Au ratio of 40 when calcined at 400 °C to 2.6 at 800 °C, suggesting the migration of Au to the surface of the alloyed metal nanoparticles. It is known that when utilising a variety of oxide supports it is possible for Au-Pd nanoparticles to adopt a Au-core PdO-shell upon calcination and this may explain why Pd : Au ratio is so high when calcined at 400 °C. The decrease in Pd : Au ratio with increasing calcination temperature may be due to the breakdown of this core-shell morphology.

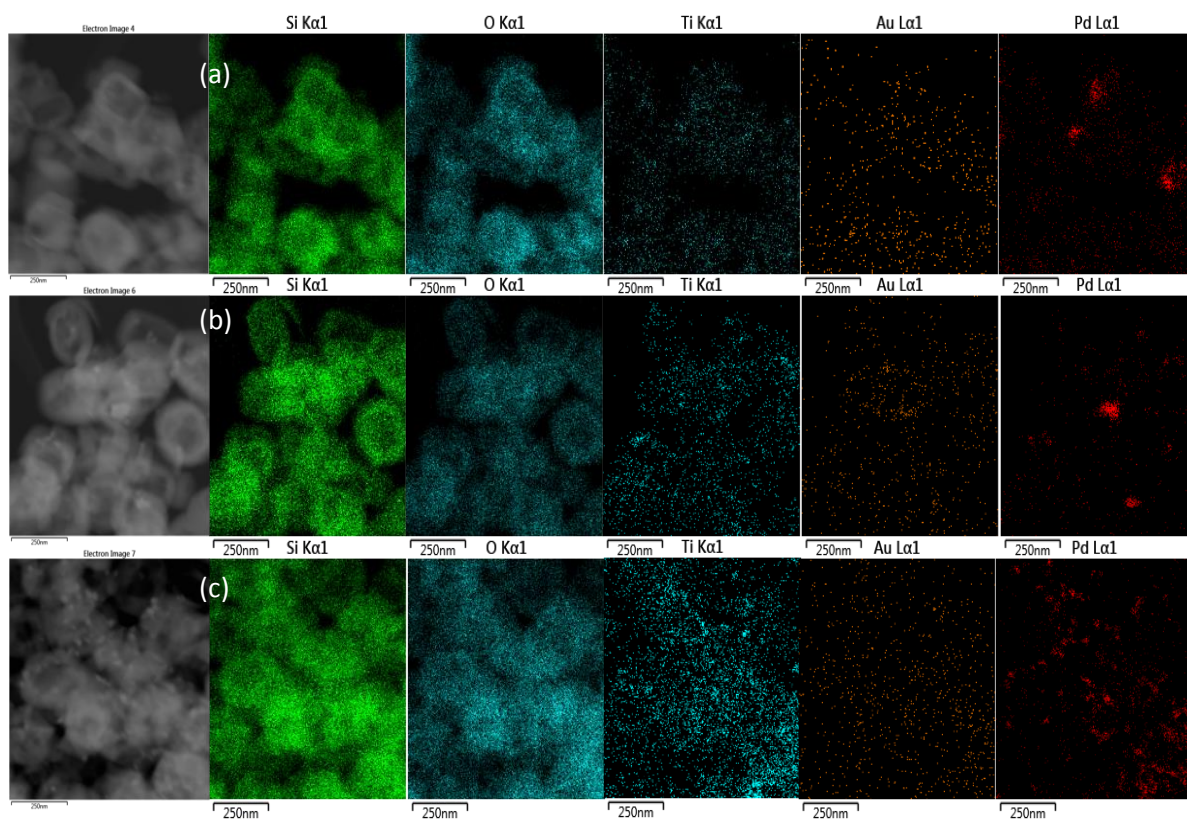
Unlike for the Pd-only supported catalysts it is not possible to investigate AuPd/TS-1 by CO chemisorption due to the need for sub-ambient temperatures when investigating Au, these facilities are not available at Cardiff University. It is suggested that a trend similar to that seen for the Pd-only catalysts would be observed for these AuPd/TS-1; where metal dispersion decreases as calcination temperature increase.

Further investigation of the effect of calcination temperature on 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 was carried out using transmission electron microscopy can be seen in Figure 5.15.



**Figure 5.15.** Transmission Electron Microscopy of 2.5 wt. % Au – 2.5 wt.% Pd / TS-1 exposed to calcination temperatures of (a) 400 °C, (b) 600 °C, (c) 800 °C (3 h, 20 OC min <sup>-1</sup>, static air).

As with the 5 wt. % Pd / TS-1 catalyst, shown in Figure 5.4, it is observed that increasing calcination temperature results in larger, less well dispersed metal nanoparticles. However, it is not possible to determine particle size distribution due to the deformation of the metal nanoparticles that is it is not possible to identify individual nanoparticles. Further investigation by STEM-EDX is observed in Figure 5.16.

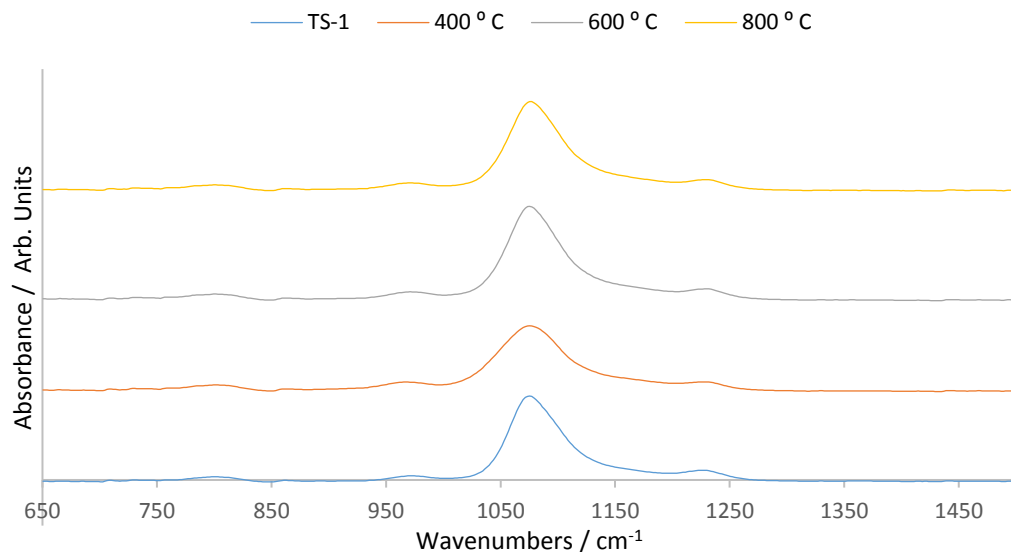


**Figure 5.16.** STEM-EDX analysis of 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 calcined at (a) 400 °C, (b) 600 °C, (c) 800 °C. Si (Green), O (Blue), Ti (Blue), Au (Orange), Pd (Red).

It is possible that the presence of Au limits the formation of larger Pd nanoparticles at these calcination temperatures. This may either be through alloying of the two metals or due to the presence of additional  $\text{Cl}^-$  anions, found in the Au precursor,  $\text{HAuCl}_4$ . Indeed, Hutchings and co-workers have previously reported that  $\text{Cl}^-$  increases Pd distribution in a similar manner<sup>12</sup>.

Further investigation into the structure of the 2.5 wt. % Au – 2.5 wt. % Pd TS-1 catalysts exposed to increasing calcination temperatures (400 – 800 °C) by FTIR can be seen in Figure 5.17



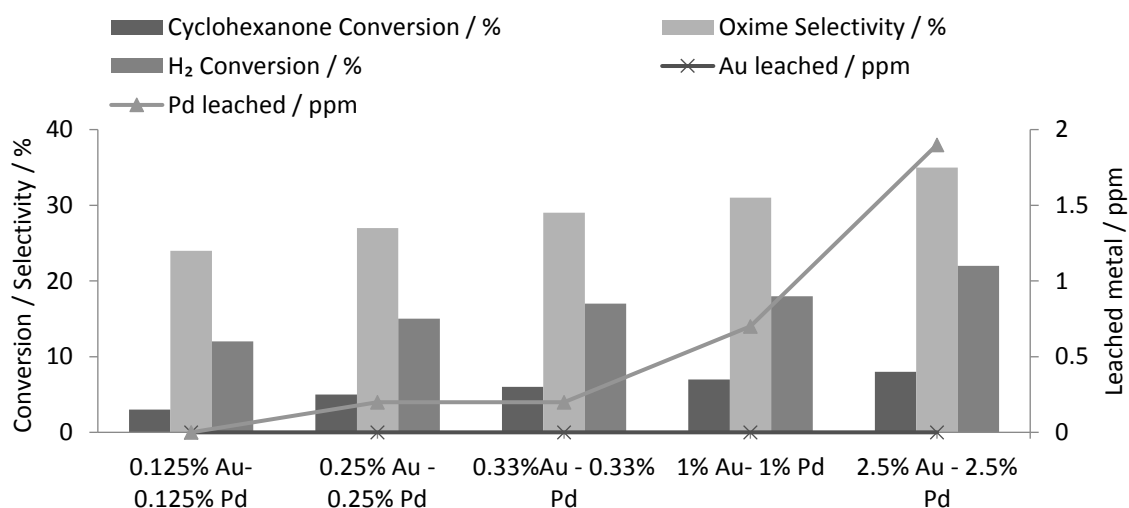


**Figure 5.17.** FTIR spectra of 2.5 wt. % Au - 2.5 wt. % Pd / TS-1 catalysts calcined at 400 – 800 °C (3 h, static air, 20 °C min<sup>-1</sup>).

Investigation by FTIR reveals no significant changes in the structure of TS-1, as with the 5 wt. % Pd / TS-1 catalysts shown in Figure 5.6.

#### 5.2.6. Investigation of the effect of total metal loading for Au-Pd catalysts for the ammoximation of cyclohexanone.

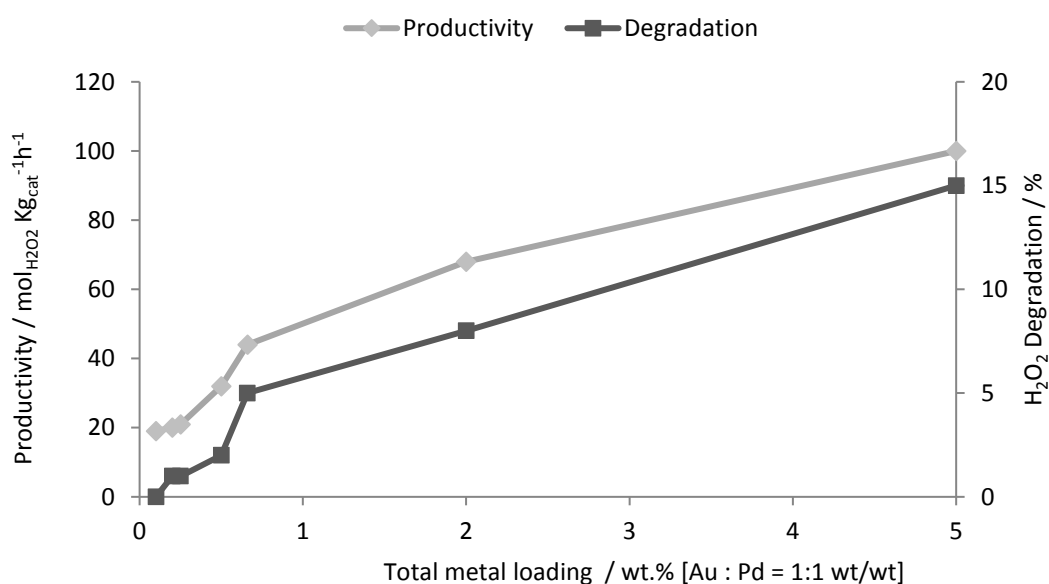
Figure 5.17 shows the effect of changing the total loading of active metal while maintaining the Au : Pd ratio at 1:1 wt/ wt on the ammoximation of cyclohexanone.



**Figure 5.17** The effect of total metal loading on the activity towards ammoximation of cyclohexanone for Au-Pd/TS-1 catalysts where Au : Pd = 1 : 1 (wt/wt).

**Reaction conditions:** Catalyst (0.05 g), cyclohexanone (0.13 g, 0.13 mmol), NH<sub>3</sub> (0.08 g, 28 wt. %, 1.3 mmol), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g H<sub>2</sub>O (66 wt. % t-BuOH), 80 °C.

It can be seen that as metal loading increases, oxime selectivity, cyclohexanone conversion and H<sub>2</sub> conversion improve, in a manner similar to that observed for the 5 wt.% Pd / TS-1 catalyst (Figure 5.1). This is attributed to increased rates of catalytic H<sub>2</sub>O<sub>2</sub> synthesis. Rates of cyclohexanone conversion are relatively low for all catalysts investigated in Figure 5.17. Interestingly, upon lowering the total metal content by a factor of 20, from 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 to 0.125 wt. % Au – 0.125 wt. % Pd / TS-1, the cyclohexanone conversion rate is only decreased by a factor of 2.6, from 8 to 3 %. Selectivity is observed to decrease across this range, from 36 at 5 wt. % metal loading to 24 % at 0.25 wt. % metal loading. As with the other two metrics used to determine catalyst efficiency (selectivity towards the oxime and cyclohexanone conversion) H<sub>2</sub> conversion also increases with total metal loading, from 12 to 22 % for 0.125 wt. % Au – 0.125 wt.% Pd / TS-1 and 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 respectively. This improvement, as with cyclohexanone conversion and oxime selectivity is ascribed to an increase in the rate of H<sub>2</sub>O<sub>2</sub> synthesis. The same catalysts were therefore assessed for H<sub>2</sub>O<sub>2</sub> synthesis and degradation with the data shown in Figure 5.18.



**Figure 5.18.** The effect of total metal loading on H<sub>2</sub>O<sub>2</sub> synthesis and degradation, for Au-Pd/ TS-1 catalysts where Au: Pd = 1: 1 wt/ wt.

**Reaction conditions:** Catalyst (0.01 g), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g MeOH + 2.9 g H<sub>2</sub>O (66 wt. % MeOH), 2 °C.

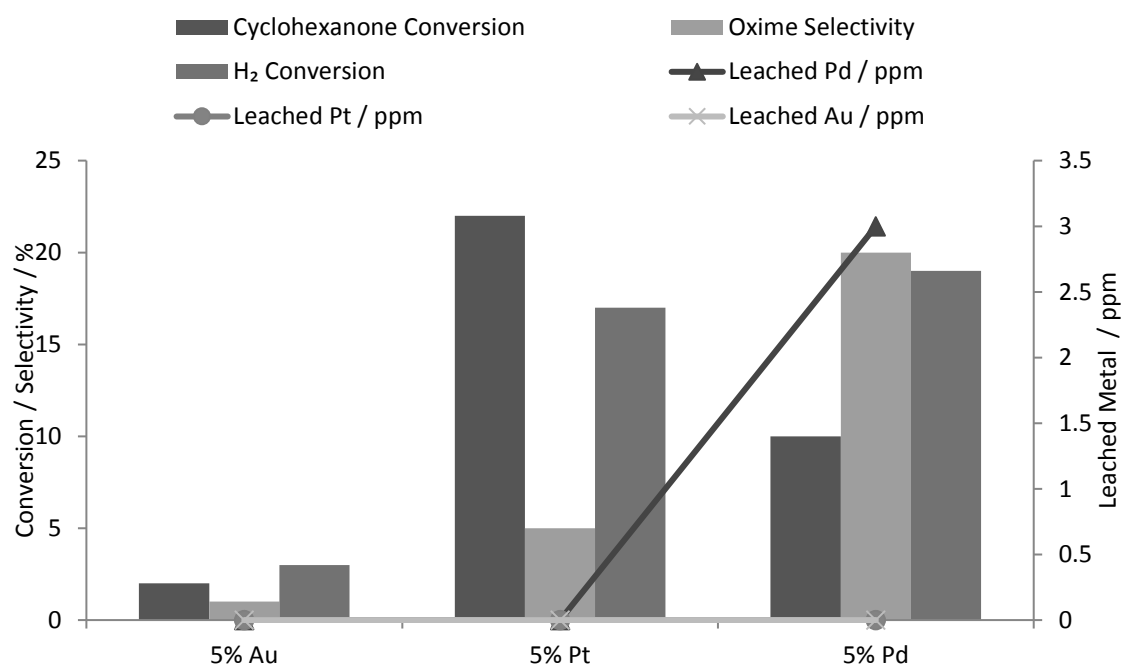
Catalytic activity towards both H<sub>2</sub>O<sub>2</sub> synthesis and degradation is observed to correlate with total metal loading. That is, as the total metal loading decreases so does catalytic activity. This has been observed previously in Section 5.2.1 for Pd loading. It is observed in Figure 5.18 that catalyst activity for the direct synthesis of H<sub>2</sub>O<sub>2</sub> increases from 19 to

100 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> as the total metal loading increases from 0.1 wt. % to 5 wt. %. A similar trend can be observed for catalytic activity towards H<sub>2</sub>O<sub>2</sub> degradation, with the rate of H<sub>2</sub>O<sub>2</sub> conversion increasing from 0 to 15 %. It is particularly interesting that the catalyst with the lowest total metal loading (0.05 wt. % Au – 0.05 wt. % Pd / TS-1) shows no activity towards the degradation of H<sub>2</sub>O<sub>2</sub>, over the timescale investigated (30 min). As such the catalyst is highly selective towards H<sub>2</sub>O<sub>2</sub>, although when compared to catalysts with higher metal loadings the activity towards H<sub>2</sub>O<sub>2</sub> synthesis is relatively low.

#### 5.2.7. Mono – bi – and tri-metallic Pd / Pt / Au / catalysts supported on TS-1 for the ammoximation of cyclohexanone.

Previous studies by Hutchings and co-workers<sup>13</sup> have reported the activity of Pt - containing Au-Pd catalysts towards the direct synthesis of H<sub>2</sub>O<sub>2</sub>, while Strukul and co-workers have studied Pd – Pt / ZrO<sub>2</sub> – SO<sub>4</sub> for the direct synthesis of H<sub>2</sub>O<sub>2</sub><sup>14</sup>.

Preliminary studies are shown in Figure 5.19 comparing the activity of monometallic 5 wt. % Au / Pd / Pt / TS-1 catalysts for the ammoximation of cyclohexanone.



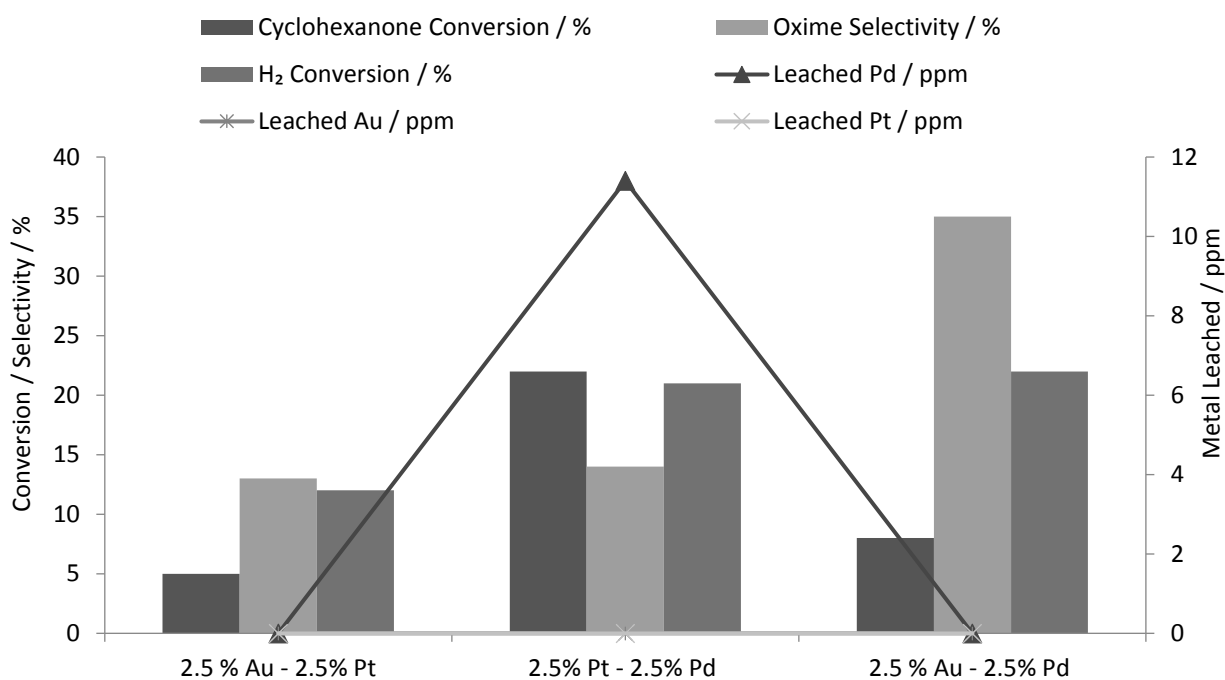
**Figure 5.19.** Monometallic Au / Pd / Pt catalysts for the ammoximation of cyclohexanone.

**Reaction conditions:** Catalyst (0.05 g), cyclohexanone (0.13 g, 1.3 mmol), NH<sub>3</sub> (0.08g, 28 wt. %, 1.3 mmol), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g H<sub>2</sub>O (66 wt. % t-BuOH), 80 °C.

It is observed, in Figure 5.19, that cyclohexanone oxime selectivity and H<sub>2</sub> conversion follows the order Pd > Pt > Au. Interestingly, the monometallic Pt catalyst affords higher rates of

conversion than Au or Pd catalysts (22 % compared to 10 and 2 % respectively) though the Pt catalysts shows lower oxime selectivity than the Pd analogue. This is attributed to the greater H<sub>2</sub> affinity displayed by Pt in comparison to Au and Pd. It is suggested that this results in an increase in unwanted hydrogenated by-products such as cyclohexanol.

Bi-metallic catalyst consisting of two component metals (Au, Pd and Pt) were also studied for the ammoximation of cyclohexanone, the results are shown in Figure 5.20.



**Figure 5.20.** Bimetallic catalysts containing Au, Pd or Pt for the ammoximation of cyclohexanone.

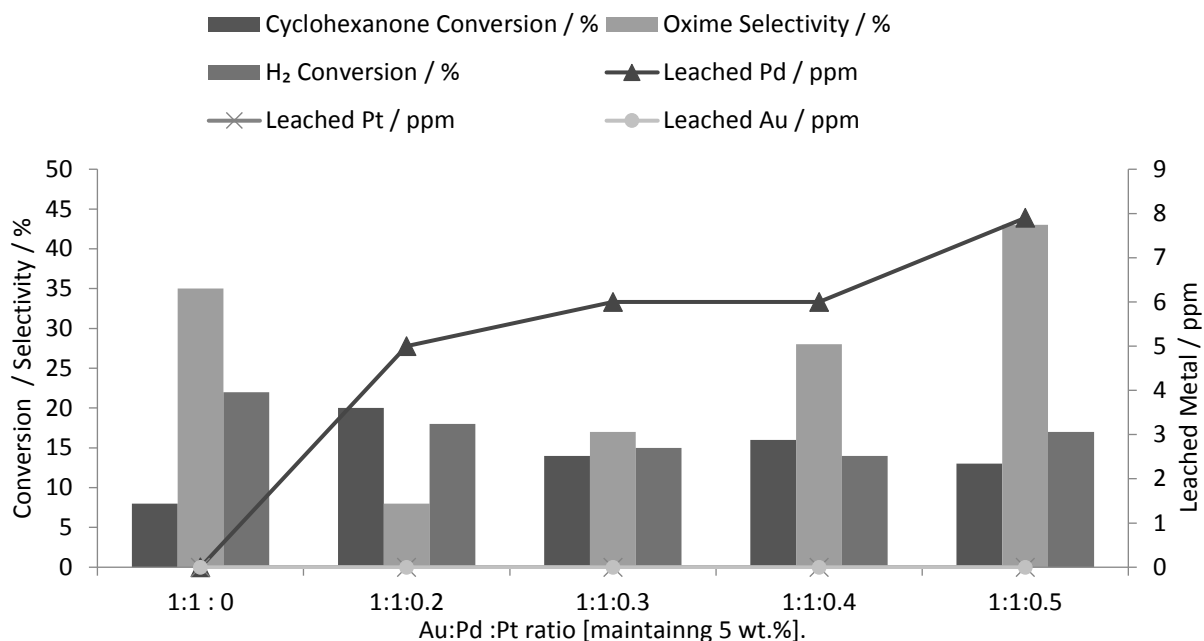
**Reaction conditions:** Catalyst (0.05 g), cyclohexanone (0.13 g, 1.3 mmol), NH<sub>3</sub> (0.08g, 28 wt. %, 1.3 mmol), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g H<sub>2</sub>O (66 wt. % t-BuOH), 80 °C.

Interestingly, even though the monometallic Au/ TS-1 catalyst shows lower rates of conversion and selectivity than the Pt analogue a combination of the two metals results in increased oxime selectivity, from 5 % for 5 wt. % Pt / TS-1 to 13 % for 2.5 wt. % Au – 2.5 Wt. % Pt / TS-1.

Comparing the bimetallic catalysts tested, the selectivity afforded by 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 exceeds that observed for 2.5 wt. % Pd- 2.5 wt. %Pt / TS-1 or 2.5 wt. %Au – 2.5 wt. % Pt / TS-1 with oxime selectivities of 35, 14 and 13 % respectively. Interestingly the cyclohexanone conversion observed over 2.5 wt. % Pd- 2.5 wt. % Pt / TS-1 is greater than observed for 2.5 wt. % Au - 2.5 wt. % Pd / TS-1, at 22 and 8 % conversion respectively. This suggests that the hydrogenation ability of the Pd- Pt / TS-1 catalyst is greater than that of the Pd- Au / TS-1 catalyst. It has been reported by Holderich and co-workers<sup>15</sup> that the addition

of Pt to Pd / TS-1 stabilises surface Pd(II)O species, an oxidation state known to favour H<sub>2</sub>O<sub>2</sub> formation . This may increase the rate of H<sub>2</sub>O<sub>2</sub> synthesis for the 2.5 wt. % Pd – 2.5 wt. % Pt / TS-1 catalyst such that it exceeds the rate of hydroxylamine formation at Ti (IV) sites, which would lead to lower oxime selectivity due to increased H<sub>2</sub>O<sub>2</sub> degradation from the reaction conditions. It is suggested that due to the harsh reaction conditions only the Ti (IV) sites in close proximity to the metal nanoparticles responsible for H<sub>2</sub>O<sub>2</sub> synthesis are involved in the formation of hydroxylamine and cyclohexanone oxime. Wang *et.al.*<sup>16</sup> have reported that H<sub>2</sub>O<sub>2</sub> productivity strongly depends on the Pt : Pd ratio. They report that increasing the Pt to Pd ratio is deleterious to the rate of H<sub>2</sub>O<sub>2</sub> synthesis. Further work is required to determine how the Pd : Pt ratio effects catalytic activity for cyclohexanone oxime synthesis and to assess the rates of H<sub>2</sub>O<sub>2</sub> synthesis and degradation over the mono- and bi-metallic catalysts in Figures 5.19 and 5.20.

Assessment of the catalytic activity of mono- and bi- metallic catalysts comprising of Au, Pd or Pt in Figures 5.19 and 5.20 provides key information as to potential routes to designing a TS-1 supported catalyst which is not only active for the ammoximation of cyclohexane with *in situ* H<sub>2</sub>O<sub>2</sub> generation but also selective towards cyclohexanone oxime as the favoured reaction product. Specifically; high rates of cyclohexanone conversion are favoured over Pt-containing catalysts, due to platinum's high affinity for H<sub>2</sub>, however Pt catalysts show low oxime selectivity. Meanwhile Pd- catalysts show appreciable oxime selectivity, at the expense of substrate conversion. Finally addition of Au, which itself shows low rates of substrate conversion, as a second metal with Pt- or Pd increases both oxime selectivity and, in the case of Pd, stabilises the active phase towards chemical leaching. To determine whether the positive effects of Au, Pd and Pt might be combined in a cumulative fashion, trimetallic TS-1 catalysts comprising of Au- Pd (1: 1 wt/wt) and low loadings of Pt were prepared and catalytic data for these is shown in Figure 5.21.

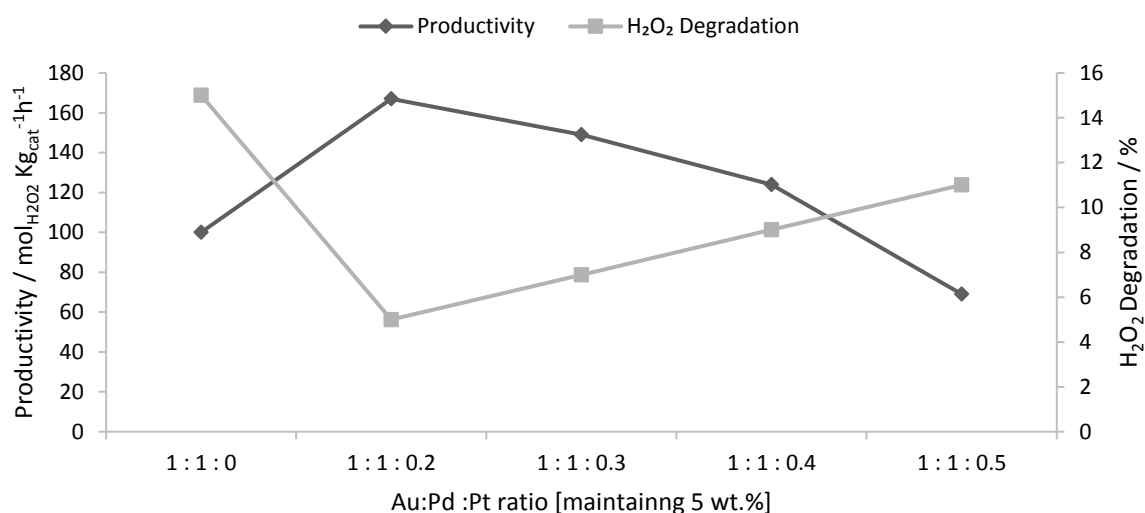


**Figure 5.21** Tri-metallic catalysts of varying metal formulations comprising Au, Pd and Pt (total metal loading = 5 wt. %) for the ammoxidation of cyclohexanone.

**Reaction conditions:** Catalyst (0.05 g), cyclohexanone (0.13 g), NH<sub>3</sub> (0.08 g, 28 wt. %), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g H<sub>2</sub>O (66 wt. % t-BuOH), 80 °C.

It is observed that the addition of Pt ( $\leq 0.45$  wt. %) along with Au and Pd (Au : Pd = 1 : 1 wt/wt, total metal loading = 5 wt. %) dramatically decreases oxime selectivity, from 35% for 2.5wt. % Au – 2.5 wt.% Pd / TS-1 to 8% selectivity for 2.4 wt.% Au – 2.4 wt.% Pd – 0.2 wt.% Pt / TS-1 (Au : Pd : Pt wt.% ratio of 1 : 1 : 0.08). This drop in oxime selectivity coincides with a substantial increase in cyclohexanone conversion from 8 % for 2.5 wt. % Au 2.5 wt. % Pd/TS-1 to 20 % for 2.4 wt. % Au 2.5 wt. % Pd 0.2 wt. % Pt/TS-1. Further increasing of the wt. % loading of Pt (at a total metal loading of 5 wt. %) is found to have a beneficial effect upon catalyst performance. As shown in Figure 5.21, the trimetallic catalyst 2 wt. % Au 2 wt. % Pd 1 wt. % Pt/ TS-1 shows optimal catalytic performance, affording 13 % substrate conversion, 43 % oxime selectivity and 17 % H<sub>2</sub> conversion. However, with increasing Pt content/ oxime selectivity, Pd leaching also increases. No apparent leaching of Au or Pt was detected.

The poor selectivity observed in Figure 5.21 at low Pt loadings might be attributed a beneficial effect of Pt upon the catalytic activity towards the direct synthesis of H<sub>2</sub>O<sub>2</sub> relative to Au- Pd alone. To further explore this, trimetallic catalysts were assessed for H<sub>2</sub>O<sub>2</sub> synthesis and degradation reactions, the results are shown in Figure 5.22.



**Figure 5.22.** Tri-metallic catalysts of varying metal formulations comprising Au, Pd and Pt (total metal loading = 5 wt. %) for the direct synthesis and degradation of H<sub>2</sub>O<sub>2</sub>.

**Reaction conditions:** 5 wt. % Pd / TS-1 (0.01 g), total pressure 580 psi, H<sub>2</sub>/O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g MeOH + 2.69 g H<sub>2</sub>O (66 wt. % MeOH), 2°C.

The effect of varying the Pt content in AuPdPt / TS-1 trimetallic catalysts, while maintaining Au : Pd ratio at 1 : 1, on the rates of H<sub>2</sub>O<sub>2</sub> synthesis and degradation is shown in Figure 5.22. As can be observed, the small addition of Pt reduces the extent of H<sub>2</sub>O<sub>2</sub> degradation when compared to the Au-Pd catalyst significantly, from 15 % to for the Au-Pd / TS-1 catalyst to 5% when 0.2 wt. % Pt is included. This corresponds with an increase in the rate of H<sub>2</sub>O<sub>2</sub> synthesis, from 100 to 167 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>. This is in keeping with the findings of Pritchard *et.al.*<sup>13</sup> who investigated the effect of Pt introduction into Au-Pd supported on CeO<sub>2</sub>. Pritchard *et.al.*<sup>13</sup> reports that the introduction of 0.1 wt. % Pt into a Au Pd/CeO<sub>2</sub> catalyst decreased the rate of H<sub>2</sub>O<sub>2</sub> degradation from 145 to 76 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>, while the rate of H<sub>2</sub>O<sub>2</sub> synthesis increased significantly from 68 to 109 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup>. Further investigation by Pritchard *et.al.*<sup>13</sup> has revealed that the introduction of Pt increased the surface ratio of Pd : Au from a value of 7 for the 2.5 wt. % Au – 2.5 wt. % Pd / CeO<sub>2</sub> catalyst (similar to the value reported herein for the 2.5 wt. % Au – 2.5 wt. % Pd TS-1 catalyst) to 58 for the 2.4 wt. % Au – 2.4 wt. % Pd – 0.2 wt.% Pt / CeO<sub>2</sub> catalyst, with a corresponding increase in catalytic activity towards the direct synthesis of H<sub>2</sub>O<sub>2</sub> from 68 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> for the 2.5 wt. % Au – 2.5 wt. % Pd / CeO<sub>2</sub> catalyst to 170 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> for the 2.4 wt. % Au – 2.4 wt. % Pd – 0.2 wt.% Pt / CeO<sub>2</sub> catalyst. A similar improvement can be seen in Figure 5.22, where catalytic activity towards H<sub>2</sub>O<sub>2</sub> formation increases from 100 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> for the 2.5 wt. % Au – 2.5 wt. % Pd TS-1 catalyst to 167 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> for the 2.4 wt. % Au – 2.4 wt. % Pd – 0.2 wt.% Pt / TS-1

catalyst. Investigation by XPS (Appendix 5.3 Table A.3) indicates that a similar phenomenon is observed as that reported by Pritchard *et.al.*<sup>13</sup> It is observed that the introduction of a small amount of Pt increases to Pd : Au ratio from 7 for the 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 catalyst to 34 for the catalyst. Further introduction of Pt results in a slight decrease in the Pd : Au ratio and a corresponding decrease in catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis, as observed in Figure 5.22 Again this is in keeping with the work of Pritchard *et.al.*<sup>13</sup> who report that ‘the addition of Pt to AuPd nanoparticles significantly affect the surface composition’ and that the presence of Pt results in the improvement off electronic effects through the formation of core-shell structures. It is suggested that a similar effect is observed herein with the addition of Pt to AuPd / TS-1.

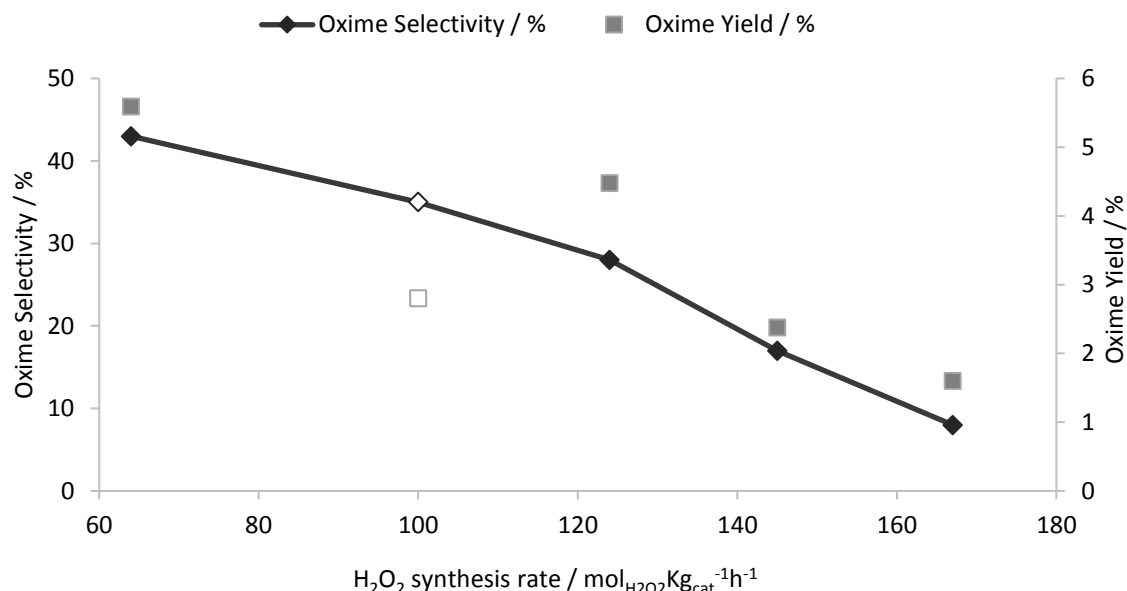
Increasing the Pt content affects a decrease in activity for H<sub>2</sub>O<sub>2</sub> synthesis of whilst also increasing the rate of H<sub>2</sub>O<sub>2</sub> degradation. Catalyst productivity for H<sub>2</sub>O<sub>2</sub> synthesis is observed to decrease from 167 to 69 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> as the Pt content increases from 0.2 to 1 wt %, while maintaining Au : Pd ratio at 1:1. The rate of H<sub>2</sub>O<sub>2</sub> degradation increases across this range, from 5 to 11 %. Interestingly, the incorporation of small amounts of Pt ( $\leq 0.45$ wt %) is observed to increase catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis beyond that of 2.5% Au – 2.5% Pd / TS-1 while H<sub>2</sub>O<sub>2</sub> degradation activity is observed to be lower than the bi-metallic catalyst. These findings correlate well with the work of Wang *et.al.*<sup>16</sup>, who reported that an optimal ratio of Pt : Pd is required to improve activity towards H<sub>2</sub>O<sub>2</sub> synthesis, and that above this ratio, activity towards the formation of H<sub>2</sub>O<sub>2</sub> decreases<sup>16</sup>.

It is possible to relate the effect of Pt content on catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis and activity for cyclohexanone ammoximation. With increasing Pt content, catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis decreases. This corresponds with decreased cyclohexanone conversion and increased oxime selectivity / an improved mass balance. Increasing selectivity suggests that H<sub>2</sub>O<sub>2</sub> plays a role in undesirable further reactions which convert cyclohexanone oxime to nitrocyclohexane which has been reported by Cesana *et.al.*<sup>17</sup>

At lower rates of H<sub>2</sub>O<sub>2</sub> synthesis the Ti(IV) sites of the support are able to activate a greater proportion of the synthesised H<sub>2</sub>O<sub>2</sub>, thereby increasing the selectivity with which H<sub>2</sub>O<sub>2</sub> is utilised in cyclohexanone oxime formation. Of course not all the H<sub>2</sub>O<sub>2</sub> that is synthesised will be utilised in hydroxylamine and in turn cyclohexanone oxime formation due to the harsh reaction conditions utilised and the activity of the catalyst towards H<sub>2</sub>O<sub>2</sub> degradation. However by maintaining a H<sub>2</sub>O<sub>2</sub> synthesis rate similar to that of hydroxylamine formation it is possible to increase selectivity toward the oxime and utilise H<sub>2</sub> in a more selective manner.



The observed rate of  $\text{H}_2\text{O}_2$  synthesis over 2.5 wt. % Au -2.5 wt. % Pd/TS-1 and trimetallic catalysts (from Figure 5.22 and corresponding oxime yields / selectivities are shown in Figure 5.23.



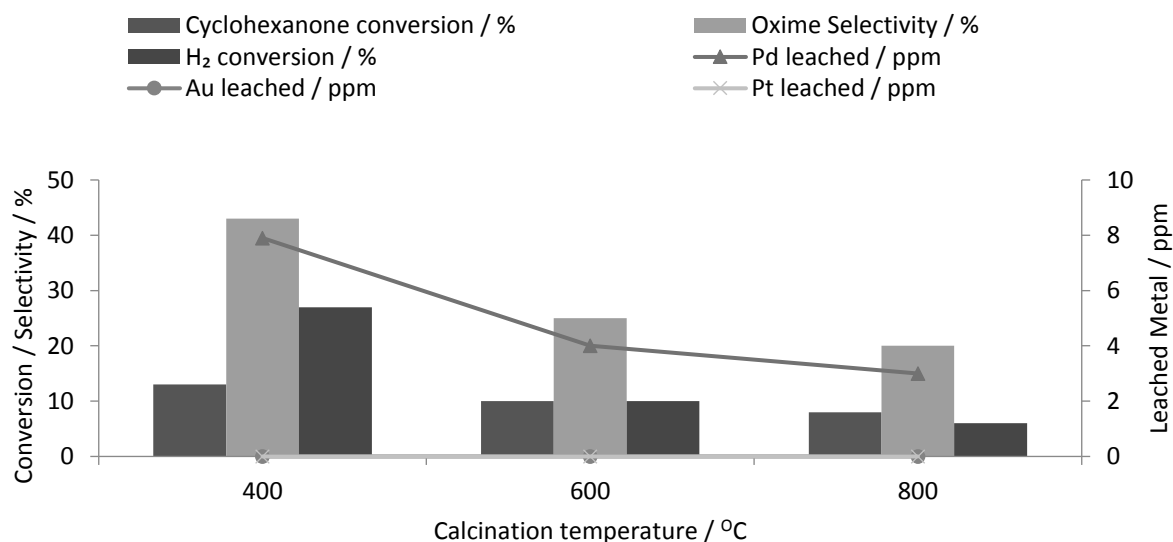
**Figure 5.23.** A plot of  $\text{H}_2\text{O}_2$  synthesis rate versus oxime selectivity and yield constructed using data for trimetallic catalysts from Figures 5.21 and 5.22.  $\diamond$  and  $\square$  represent 2.5 wt. % Au - 2.5 wt. % Pd / TS-1.

Oxime selectivity is shown in Figure 5.23 to decrease linearly with an increase in the observed rate of  $\text{H}_2\text{O}_2$  synthesis over the same catalysts. This correlates well with decreasing Pt loading (where applicable). At the same time oxime yield decreases and this is due to decreasing cyclohexanone conversion. This is curious, as cyclohexanone conversion would be expected to increase with increasing  $\text{H}_2\text{O}_2$  concentration, which suggests that mass transfer limitations are suppressing the rate of reaction.

To better understand the structure of Pt containing tri-metallic catalysts, they were analysed by XRD. Diffractograms in Appendix 5.1, Figure A5 do not indicate the presence of either PdO or Pt phases, suggesting that these metals present on the surface as nanoparticles below the XRD detection limit of 5 nm. This suggests that co-impregnation of Pt with Au- Pd does not affect a significant growth in particle size and therefore metal nanoparticle growth cannot be ascribed as the reason why catalyst activity decreases with increasing Pt content.

### 5.2.8. The effect of calcination temperature on 2 wt. % Au – 2 wt. % Pd – 1 wt. % Pt / TS-1 activity towards the ammoximation of cyclohexanone.

The effect of calcination temperature on catalytic activity towards the ammoximation of cyclohexanone is shown in Figure 5.24.

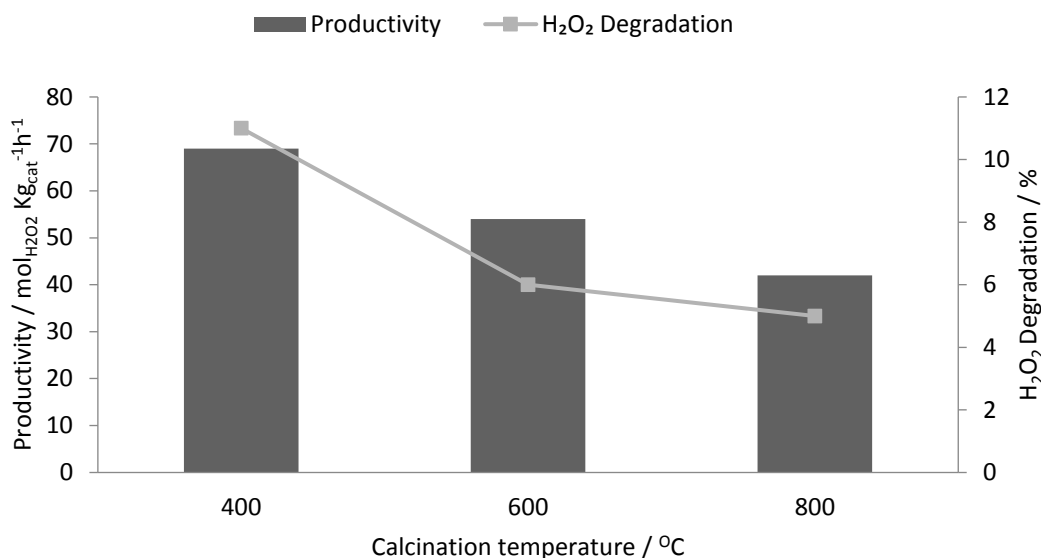


**Figure 5.24** Effect of calcination temperature on the catalytic performance of 2 wt. % Au – 2 wt. % Pd – 1 wt. % Pt / TS-1 for the ammoximation of cyclohexanone.

**Reaction conditions:** Catalyst (0.05 g), cyclohexanone (0.13 g, 1.3 mmol), NH<sub>3</sub> (0.08 g, 28 wt %, 1.3 mmol), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g H<sub>2</sub>O (66 wt % t-BuOH), 80 °C.

As previously shown for 5 wt. % Pd / TS-1 (Figure 5.7) and 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 (Figure 5.13), a decrease in both cyclohexanone conversion and oxime selectivity is observed as the calcination temperature increases from 400 to 800 °C. A significant decrease in oxime selectivity is observed across this range, from 43 to 20 %. When compared with the mono- and bi-metallic catalysts, the decrease in activity is not as pronounced, with cyclohexanone conversions of 13 and 8 % following calcination at 400 and 800 °C respectively.

To rationalise these trends, the same catalysts were assessed for H<sub>2</sub>O<sub>2</sub> synthesis and degradation reactions. This data is shown in Figure 5.25.



**Figure 5.25** The effect of calcination temperature on H<sub>2</sub>O<sub>2</sub> synthesis and degradation activity of 2 wt. % Au – 2 wt. % Pd – 1 wt. % Pt / TS-1.

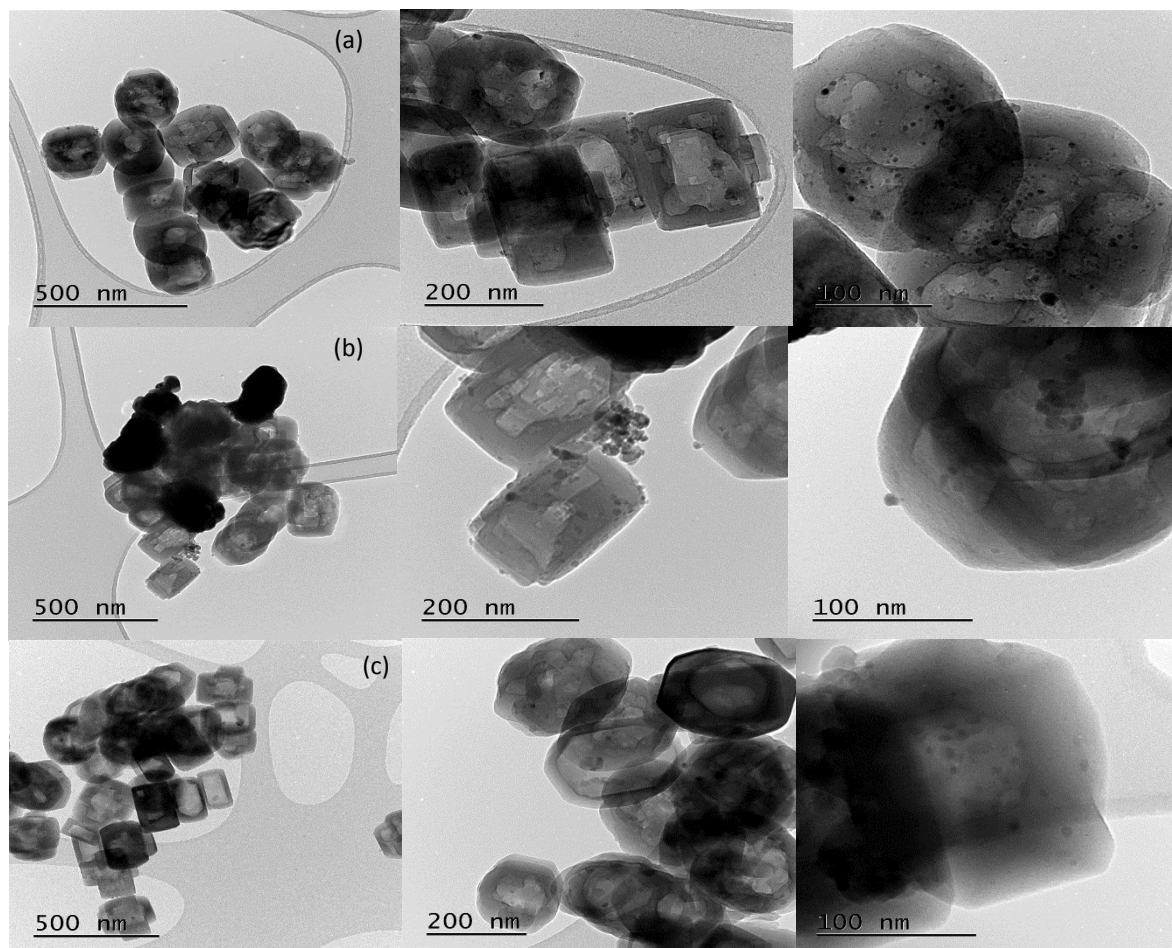
**Reaction conditions:** Catalyst (0.01 g), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g MeOH + 2.69 g H<sub>2</sub>O (66 wt. % MeOH), 2°C.

As previously observed for 5 wt. % Pd/ TS-1 and 2.5 wt. % - 2.5 wt. % Pd / TS-1, increasing the calcination temperature leads to a decrease in catalytic activity for the direct synthesis and degradation of H<sub>2</sub>O<sub>2</sub>. However in comparison to 5 wt. % Pd / TS-1 and 2.5 wt. % Au – 2.5 wt. % Pd the loss in activity towards H<sub>2</sub>O<sub>2</sub> synthesis is less pronounced, with a loss in activity of *ca.* 40 % between upon increasing the calcination temperature from 400 to 800 °C. This is compared with relative decreases in rate of 90 and 70 % for 5 wt. % Pd/ TS-1 and 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 catalyst respectively, across the same temperature range. As with the mono- and bi-metallic catalysts, this loss in catalytic activity is ascribed to an increase in nanoparticle size as eluded to by the development of reflections associated with these metals when studied by XRD (Table 5.2) (diffractograms shown in Appendix 5.3 Figure A3). In particular the increased intensity of the reflection at 40 and 67 ° associated with Pt which is observed at higher calcination temperatures (600 and 800 °C) but not at 400 °C, while the reflection at 38 ° associated with Au is observed regardless of calcination temperature. The development in reflections associated Pt correlates well with analysis by XPS. It is seen in Appendix 5.3 that atomic composition of Pt decreases 0.27 to 0.03 At. % when calcination temperature increases from 400 to 800 °C.

Furthermore as previously determined for 5 wt. % Pd/ TS-1 and 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 there is a significant loss in TS-1 crystallinity upon metal incorporation and calcination, shown in Table 5.2 with the crystallinity of the catalyst calcined at 800 °C seen to be 33.8 % of that of the untreated support. Further investigation in to the TS-1 support by XRD reveals the development of a TiO<sub>2</sub> rutile phase (Appendix 5.2, Table A.1) and this is supported by analysis by XPS (Appendix 5.3, Table A.2)

which indicates a dramatic change in the Si : Ti ratio from 88.2 when the 2 wt.% Au – 2 wt. % Pd -1 wt. % Pt / TS-1 catalyst is calcined at 400 °C to 65.3 when calcined at 800 °C.

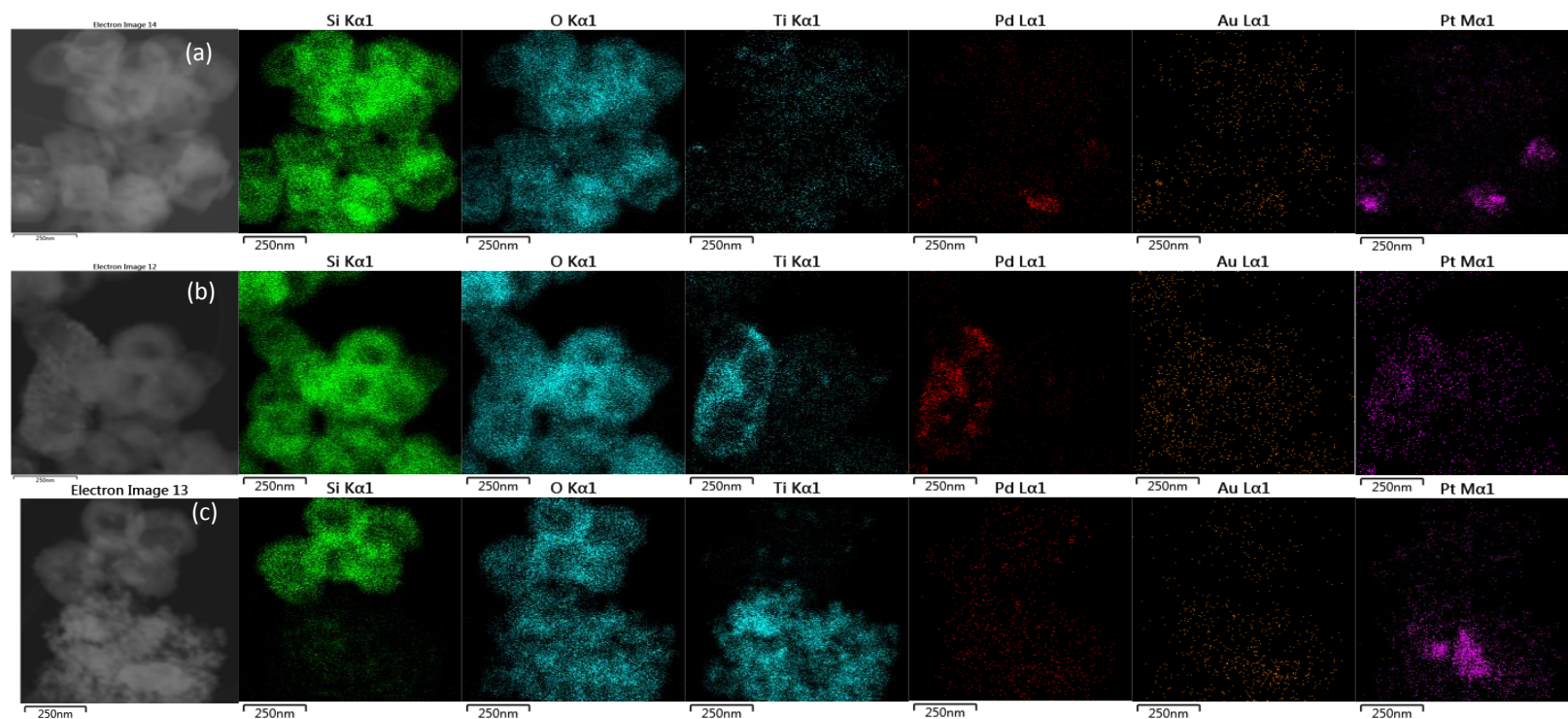
Further investigation by TEM and STEM-EDX into the effect of calcination temperature on 2 wt. % Au – 2. Wt % Pd. 1 wt % Pt / TS-1 can be seen in Figures 5.26 and 5.27.



**Figure 5.26.** Transmission Electron Microscopy of 2 wt. % Au – 2 wt. % Pd – 1 wt. % Pt / TS-1 calcined at (a) 400 °C (b) 600 °C and (c) 800 °C (3 h, 20 °C min<sup>-1</sup>, static air).

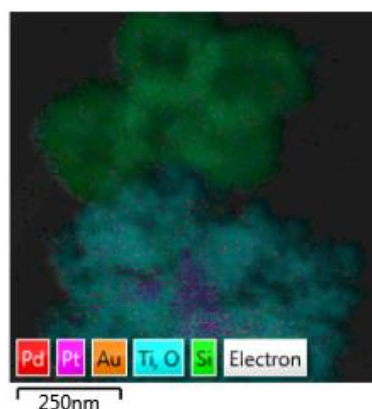
Investigation by TEM indicates the sintering of metal nanoparticles as calcination temperature increases, as with 5 wt. % Pd / TS-1 and 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 it is not possible to determine particle size distribution due to a lack of discernible, individual metal nanoparticles, which is caused by deformation of the metal nanoparticles as calcination temperature increases. As such there are not a statistically relevant number of individual nanoparticles present to determine particle size distribution.

The effect of calcination temperature was also investigated by STEM-EDX, with the results observed in Figure 5.27.



**Figure 5.27.** STEM-EDX analysis of 2 wt. % Au – 2 wt. % Pd – 1 wt. % Pt / TS-1 calcined at (a) 400 °C, (b) 600 °C, (c) 800 °C. Si (Green), O (Blue), Ti (Blue), Au (Orange), Pd (Red), Pt (Purple).

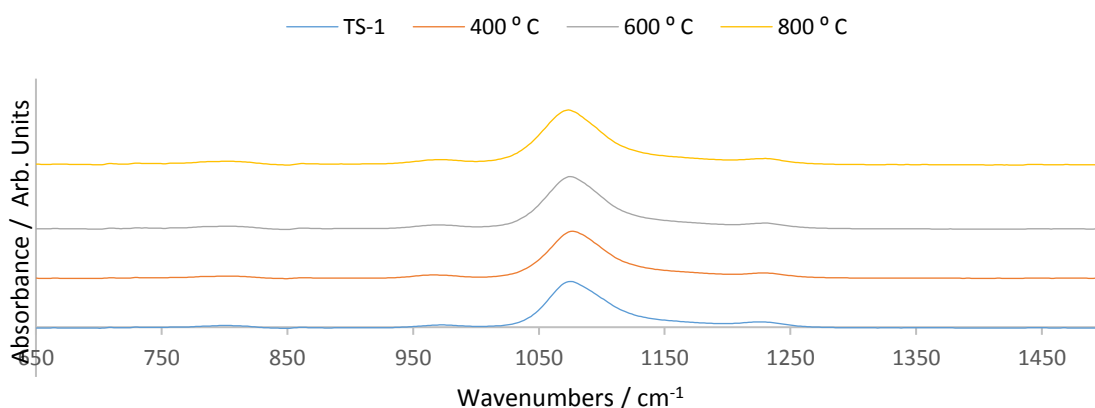
Investigation by STEM-EDX corroborates analysis by XRD, which indicated a decrease in dispersion of Pd, Au and Pt with increasing calcination temperature, particularly with regards to Pt and Au. As discussed previously investigation of the 2 wt. % Au – 2 wt. % Pd – 1 wt. % Pt / TS-1 catalyst calcined at 800 °C by XRD indicates the development of the TiO<sub>2</sub> rutile phase (6 %), however it should be noted that phase identification is semi-quantitative. This is substantiated via investigated by STEM-EDX, shown in Figure 5.28.



**Figure 5.28.** STEM-EDX analysis of 2 wt. % Au – 2 wt. % Pd – 1 wt. % Pt / TS-1 catalyst calcined at 800 °C showing development of the TiO<sub>2</sub> rutile phase.

It can be observed that two distinct phases appear upon calcination of the 2 wt. % Au – 2 wt. % Pd – 1 wt. % Pt / TS-1 catalyst at 800 °C; a Ti phase (blue) and a Si phase (green). This supports investigation by XRD which shows both a loss in crystallinity of the support upon increasing calcination temperature (Table 5.2) and development of a TiO<sub>2</sub> phase (Appendix 5.2, Table A.1).

Further investigation by FTIR can be seen in Figure 5.29.



**Figure 5.29.** FTIR spectra of 2 wt. % Au – 2 wt. % Pd – 1 wt. % Pt / TS-1 catalysts calcined at 400 – 800 °C (3 h, static air, 20 °C min<sup>-1</sup>).

As with the 5 wt. % Pd / TS-1 and 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 catalysts there is no loss in the structure of TS-1 upon metal incorporation and exposure to calcination temperatures ranging from 400 – 800 °C.

In conclusion the loss in activity for H<sub>2</sub>O<sub>2</sub> synthesis and cyclohexanone ammoximation reactions following calcination at 600 and 800 °C, as represented in Figures 5.24 and 5.25, is attributed to the increase in metal nanoparticle size and a decrease in crystallinity of TS-1. It is observed that while PdO is not detected by XRD, suggesting the presence of PdO as nanoparticles smaller than the detection limit of XRD (5 nm), the average particle sizes of Au and Pt by XRD are 50 and 28.7 nm respectively when 2 wt. % Au – 2 wt. % Pd – 1 wt. % Pt / TS-1 is calcined at 800 °C

#### 5.2.9. The effect of calcination temperature of 5 wt. % Au-Pd-Pt / TS-1 catalysts for the ammoximation of cyclohexanone via direct synthesis of H<sub>2</sub>O<sub>2</sub>.

It is shown above that the incorporation of Pt into a Au-Pd catalyst can improve catalyst selectivity towards cyclohexanone oxime when the loading of Pt is relatively high (1 wt. %). The effect which Pt loading and calcination temperature have on catalytic activity for cyclohexanone ammoximation and the direct synthesis and degradation of H<sub>2</sub>O<sub>2</sub> is therefore of great interest.

It has been shown in Figure 5.25 that the decrease in catalytic activity for H<sub>2</sub>O<sub>2</sub> synthesis, observed when increasing calcination temperature from 400 to 800 °C, is far greater for 5 wt. % Pd/ TS-1 and 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 than for 2 wt. % Au – 2 wt. % Pd – 1 wt. % Pt / TS-1. To further study the apparent enhanced stability of trimetallic AuPdPt / TS-1 catalysts to high temperature calcination, the effect of Pt content was studied whilst maintaining a Au : Pd ratio of 1:1 wt/wt and a total metal loading at 5 wt. %. The ability of Pt to stabilise catalyst activity with increasing calcination temperature is shown in Table 5.3.

**Table 5.3.** The observed catalytic performance and metal leaching of trimetallic AuPdPt/ TS-1 catalysts of varying metal formulations and following differing calcination treatments.

wt. % Au	wt. % Pd	wt. % Pt	Calcination Temperature / °C	Cyclohexanone Conversion / %	Oxime Selectivity / %	Oxime Yield/ %	Au leached / ppm	Pd leached / ppm	Pt leached / ppm
2.5	2.5	0	400	8	35	2.8	n.d	3	n.d
			600	4	15	0.6	n.d	0.4	n.d
			800	2	9	0.2	n.d	0.2	n.d
2.4	2.4	0.2	400	20	8	1.6	nd	2	n.d
			600	14	5	0.7	n.d	1	n.d
			800	4	4	0.48	n.d	1	n.d
2.35	2.35	0.3	400	18	12	2.16	n.d	2	n.d
			600	13	9	1.17	n.d	1	n.d
			800	11	7	0.77	n.d	1	n.d
2.28	2.28	0.44	400	16	14	2.24	n.d	3	n.d
			600	11	13	1.43	n.d	3	n.d
			800	10	11	1.1	n.d	1	n.d
2	2	1	400	13	43	5.59	n.d	7.9	n.d
			600	10	25	2.5	n.d	4	n.d
			800	8	20	1.6	n.d	3	n.d

**Reaction Conditions:** Catalyst (0.05 g), cyclohexanone (0.13 g, 1.3 mmol), NH<sub>3</sub> (0.08 g, 28 wt %, 1.3 mmol), total pressure 580 psi, H<sub>2</sub>/ O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g H<sub>2</sub>O (66 wt % t-BuOH), 80 °C  
n.d signifies not detected.

It was previously shown in Figure 5.21 that, for catalysts calcined at 400 °C, cyclohexanone conversion generally decreases and oxime selectivity increases with increasing Pt content. Data in Table 5.3 shows that this trend holds true when catalysts are calcined at a temperature with the range of 400 – 800 °C, regardless of Pt content. Meanwhile, increasing calcination temperature has previously been shown to result in the formation of larger metal nanoparticles on the surface of the TS-1 support (Sections 5.2.2 and 5.2.5). An increased population of larger metal nanoparticles, which are suggested to be less active towards the direct synthesis and degradation of H<sub>2</sub>O<sub>2</sub>, is consistent with trends shown in Table 5.3. To determine whether Pt loading and calcination temperature significantly effect H<sub>2</sub>O<sub>2</sub> synthesis and degradation rates, catalysts were assessed for these reactions and the data is shown in Table 5.4.



**Table 5.4.** The performance of trimetallic AuPdPt catalysts for H<sub>2</sub>O<sub>2</sub> synthesis and degradation reactions as a function of Pt loading and calcination temperature.

wt. % Au	wt. % Pd	wt. % Pt	Calcination Temperature / °C	H <sub>2</sub> O <sub>2</sub> synthesis rate / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> Kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> (a)	H <sub>2</sub> O <sub>2</sub> degradation/ % (b)
2.5	2.5	0	400	100	15
			600	35	9
			800	30	6
2.4	2.4	0.2	400	167	5
			600	96	3
			800	63	3
2.35	2.35	0.3	400	149	7
			600	89	4
			800	59	4
2.28	2.28	0.44	400	124	9
			600	76	5
			800	55	4
2	2	1	400	69	11
			600	54	6
			800	42	5

**Reaction Conditions :** (a) **H<sub>2</sub>O<sub>2</sub> Synthesis Reaction Conditions:** Catalyst (0.01 g), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g MeOH + 2.69 g H<sub>2</sub>O (66 wt. % MeOH), 2°C.

(b) **H<sub>2</sub>O<sub>2</sub> Degradation Reaction Conditions:** Catalyst (0.01 g), MeOH (5.6 g), H<sub>2</sub>O (2.22 g), H<sub>2</sub>O<sub>2</sub> (50 wt. % 0.68 g), 5 % H<sub>2</sub>/CO<sub>2</sub> (2.9 MPa) 30min, 2 °C, 1200 rpm.

Table 5.4 demonstrates a beneficial effect of Pt content on maintaining catalytic activity towards the direct synthesis and degradation of H<sub>2</sub>O<sub>2</sub> with increasing calcination temperature. Increased Pt content reduces the deleterious effect of calcination temperature upon activity, with those catalysts containing more Pt retaining a greater percentage of their activity determined at 400 °C when calcined at higher temperatures. It is observed in Table 5.4 that by increasing the total Pt content it is possible to slow the loss in activity for H<sub>2</sub>O<sub>2</sub> synthesis. Indeed, 2.4 wt. % Au – 2.4 wt. % Pd – 0.2 wt. % Pt / TS-1 shows a 62.3 % drop in rate upon increasing the calcination temperature from 400 °C to 800 °C and this is compared with a rate decrease of only 33.1 % observed for 2 wt. % Au – 2 wt. % Pd – 1 wt. % Pt / TS-1 over the same temperature range.

However it should be noted that regardless of calcination temperature, catalytic activity towards the direct synthesis H<sub>2</sub>O<sub>2</sub> is related to Pt content, with catalysts of greater Pt content showing lower synthesis rates. As observed in Table 5.4, following calcination at 400 °C a catalyst with 0.2 wt. % Pt loading is more than twice as active for H<sub>2</sub>O<sub>2</sub> synthesis when compared to a catalyst containing 1 wt. % Pt, with rates of 167 and 69 mol<sub>H<sub>2</sub>O<sub>2</sub></sub> Kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> respectively.

With regards to H<sub>2</sub>O<sub>2</sub> degradation, those catalysts with higher Pt loadings are observed to be more active than those of lower Pt content. As can be observed in Table 5.4, following calcination at 400 °C

2 wt. % Au – 2 wt. % Pd – 1 wt. % Pt / TS-1 shows almost double the activity towards the degradation of  $\text{H}_2\text{O}_2$  when compared with 2.4 wt. % Au – 2.4 wt. % Pd – 0.2 wt. % Pt / TS-1 , with values of 11 and 5 % respectively.

### 5.3. Conclusion.

It has been shown that precious metal catalysts supported on commercial TS-1 are active for the direct synthesis of  $\text{H}_2\text{O}_2$  from  $\text{H}_2$  and  $\text{O}_2$  as well as towards the ammoximation of cyclohexanone to cyclohexanone oxime. It is observed that, unlike when oxide supports are utilised no synergistic effect is observed between Au and Pd for the direct synthesis of  $\text{H}_2\text{O}_2$ . Indeed  $\text{H}_2\text{O}_2$  synthesis rate is observed to correlate with Pd loading, with the greatest activity observed for the 5 wt. % Pd / TS-1 catalysts ( $116 \text{ mol}_{\text{H}_2\text{O}_2} \text{Kg}_{\text{cat}}^{-1} \text{h}^{-1}$ ).

Both monometallic Au, Pd and Pt catalysts have been shown to be active towards the ammoximation of cyclohexanone, with 5 wt. % Pd / TS-1 seen to offer the greatest selectivity towards cyclohexanone oxime (20 %). However the overall yield is very low, as with all catalysts investigated within in this work, at 2%. The addition of Au to a Pd only catalyst in a 1:1 ratio produces a catalyst that affords greater selectivity towards cyclohexanone oxime when compared to the mono-metallic Au and Pd catalysts despite the Pd-only catalyst showing greater activity towards the direct synthesis of  $\text{H}_2\text{O}_2$ . The improved conversion allows for a slightly improved yield of cyclohexanone oxime, compared to the 5 wt. Pd / TS-1 catalyst, at 2.8%. Table 5.5 compares catalytic activity towards  $\text{H}_2\text{O}_2$  synthesis and oxime yield.

**Table 5.5.** Activity of Au-Pd / TS-1 catalysts towards the direct synthesis of  $\text{H}_2\text{O}_2$  and the ammoximation of cyclohexanone.

Catalyst	Productivity / $\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$ <sup>(a)</sup>	Oxime yield / % <sup>(b)</sup>
5 wt. % Au / TS-1		0.1
2.5 wt. % Au – 2.5 wt. % Pd / TS-1	100	2.8
5 wt. % Pd / TS-1	116	2

**Reaction Conditions:** <sup>(a)</sup>**Direct synthesis of  $\text{H}_2\text{O}_2$ :** Catalyst (0.01 g), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 5.6 g MeOH + 2.69 g  $\text{H}_2\text{O}$  (66 wt. % MeOH), 2°C.

<sup>(b)</sup>**Ammoximation of cyclohexanone:** Catalyst (0.05 g), cyclohexanone (0.13 g, 1.3 mmol),  $\text{NH}_3$  (0.08 g, 28 wt %, 1.3 mmol), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g  $\text{H}_2\text{O}$  (66 wt % t-BuOH), 80 °C.

Further investigation into 5 wt. % Au-Pd-Pt catalysts supported on TS-1 has shown that the addition of small amounts of Pt, while maintaining the Au : Pd ratio at 1 :1 can drastically improve catalyst activity towards the direct synthesis of  $\text{H}_2\text{O}_2$ . The effect of Pt addition on the activity of Au-Pd / TS-1 catalysts towards the direct synthesis of  $\text{H}_2\text{O}_2$  and the ammoximation of cyclohexanone can be seen in Table 5.6.

**Table 5.6.** Activity of Au-Pd-Pt / TS-1 catalysts towards the direct synthesis of H<sub>2</sub>O<sub>2</sub> and the ammoximation of cyclohexanone.

Catalyst	Productivity / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> <sup>(a)</sup>	Oxime yield / % <sup>(b)</sup>
2.5 wt. % Au – 2.5 wt. % Pd / TS-1	100	2.
2.4 wt. % Au – 2.4 wt. % Pd / 0.2 wt. % Pt / TS-1	167	1.6
2.35 wt. % Au – 2.35 wt. % Pd / 0.3 wt. % Pt / TS-1	149	2.16
2.4 wt. % Au – 2.4 wt. % Pd / 0.44 wt. % Pt / TS-1	124	2.2
2 wt. % Au – 2 wt. % Pd / 1 wt. % Pt / TS-1	69	5.6

**Reaction Conditions :** <sup>(a)</sup>**Direct synthesis of H<sub>2</sub>O<sub>2</sub>:** Catalyst (0.01 g), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g MeOH + 2.69 g H<sub>2</sub>O (66 wt. % MeOH), 2°C.

<sup>(b)</sup>**Ammoximation of cyclohexanone:** Catalyst (0.05 g), cyclohexanone (0.13 g, 1.3 mmol), NH<sub>3</sub> (0.08 g, 28 wt %, 1.3 mmol), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g H<sub>2</sub>O (66 wt % t-BuOH), 80 °C.

Catalyst activity is seen to increase from 100 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> for the 2.5 wt. % Au-2.5 wt. % Pd / TS-1 catalyst to 167 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> with the incorporation of 0.2 wt.% Pt, while maintaining Au : Pd ratio at 1 : 1. However despite the high activity towards H<sub>2</sub>O<sub>2</sub> synthesis this catalyst offers very poor activity towards the ammoximation of cyclohexanone, in comparison to the Au-Pd analogue, with a oxime yield of 1.6 % observed for the 2.4 wt. % Au – 2.4 wt. % Pd – 0.2 wt. % Pt / TS-1 catalyst. By further increasing the Pt content to 1 wt. % it is observed that the rate of H<sub>2</sub>O<sub>2</sub> synthesis decreases, while the activity towards cyclohexanone ammoximation increases. Indeed the overall yield of cyclohexanone oxime is seen to be 5.6 % for the 2 wt. % Au – 2.4 wt. % Pd – 0.2 wt. % Pt / TS-1 catalyst, much lower than the other AuPd / TS-1 and AuPdPt/ TS-1 catalysts that have lower rates of H<sub>2</sub>O<sub>2</sub> synthesis.

Investigation of catalyst stability shows that under the conditions utilised active metal, in particular Pd, leaching is an issue. It has been shown previously in Chapter 4 Section 4.4 that leached Pd has no activity towards the ammoximation of cyclohexanone however catalyst stability is still considered essential. In an attempt to improve catalytic stability 5 wt. % Pd / TS-1, 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 and 2 wt. % Au – 2 wt. % Pd / 1 wt. % Pt / TS-1 were calcined at elevated temperatures, as high as 800 °C.

It has been shown that loss of metal from the support can be decreased through calcination at higher temperatures, although these catalysts are less active towards H<sub>2</sub>O<sub>2</sub> synthesis and the ammoximation of cyclohexanone. Investigation by XPS, XRD, TEM and STEM-EDX indicates the development of larger metal nanoparticles as calcination temperature increases. This is suggested to partly contribute to the decrease in catalyst activity towards the synthesis of H<sub>2</sub>O<sub>2</sub> and in turn formation of cyclohexanone oxime.

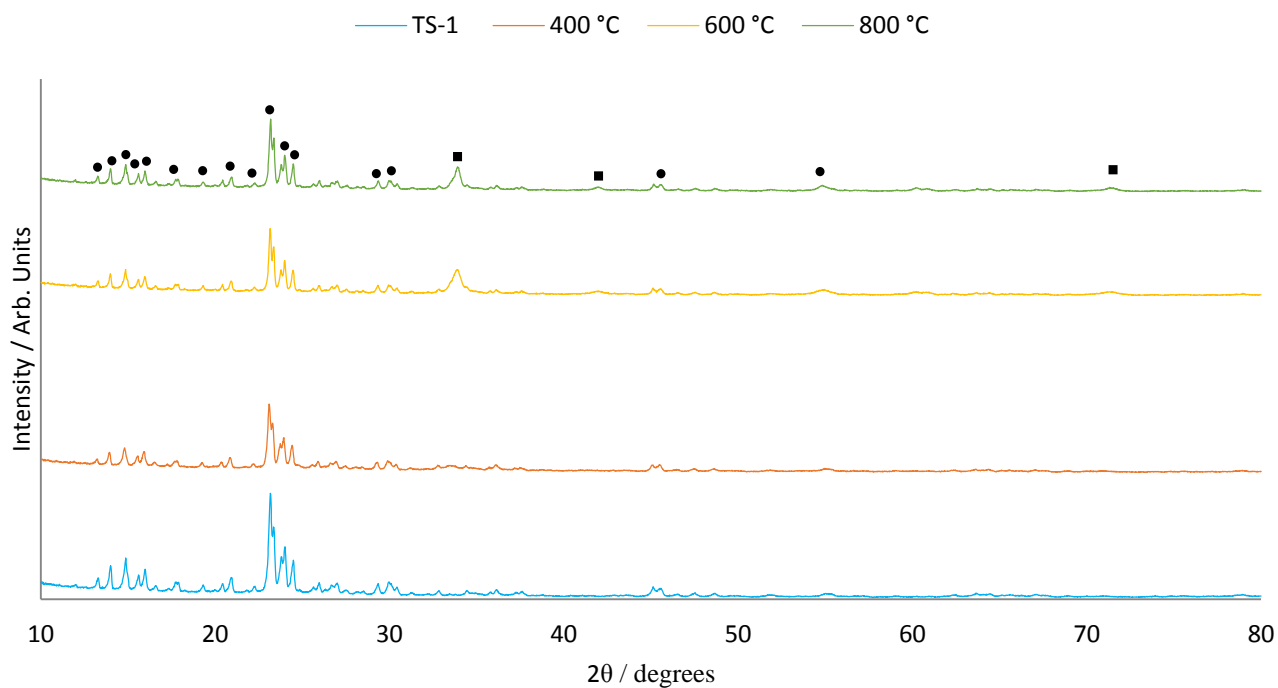
Interestingly as calcination temperature increases the Au : Pd ratio for both the 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 and 2 wt.% Au – 2 wt. % Pd – 1wt. % Pt / TS-1 catalysts decreases drastically. When analysis by XRD is also taken in to consideration it is possible to suggest that the migration of Au to the surface of the alloyed metal nanoparticles may also contribute to a loss in catalytic activity towards  $\text{H}_2\text{O}_2$  formation and cyclohexanone ammoximation.

Furthermore, it has been shown that subjecting the TS-1 support to such extreme calcination temperatures can significantly reduce its crystallinity, with the greatest loss observed for the 2 wt. % Au – 2 wt. % Pd – 1 wt. % Pt / TS-1 catalyst, with a decrease in crystallinity of 66% observed when this catalyst is calcined at 800 °C. Further investigation by XRD shows the development of the  $\text{TiO}_2$  rutile phase as calcination temperature increases, while XPS investigation of the support shows that the calcination at 800 °C leads to a significant decrease in the Si : Ti ratio, which may explain the loss in crystallinity of the support.

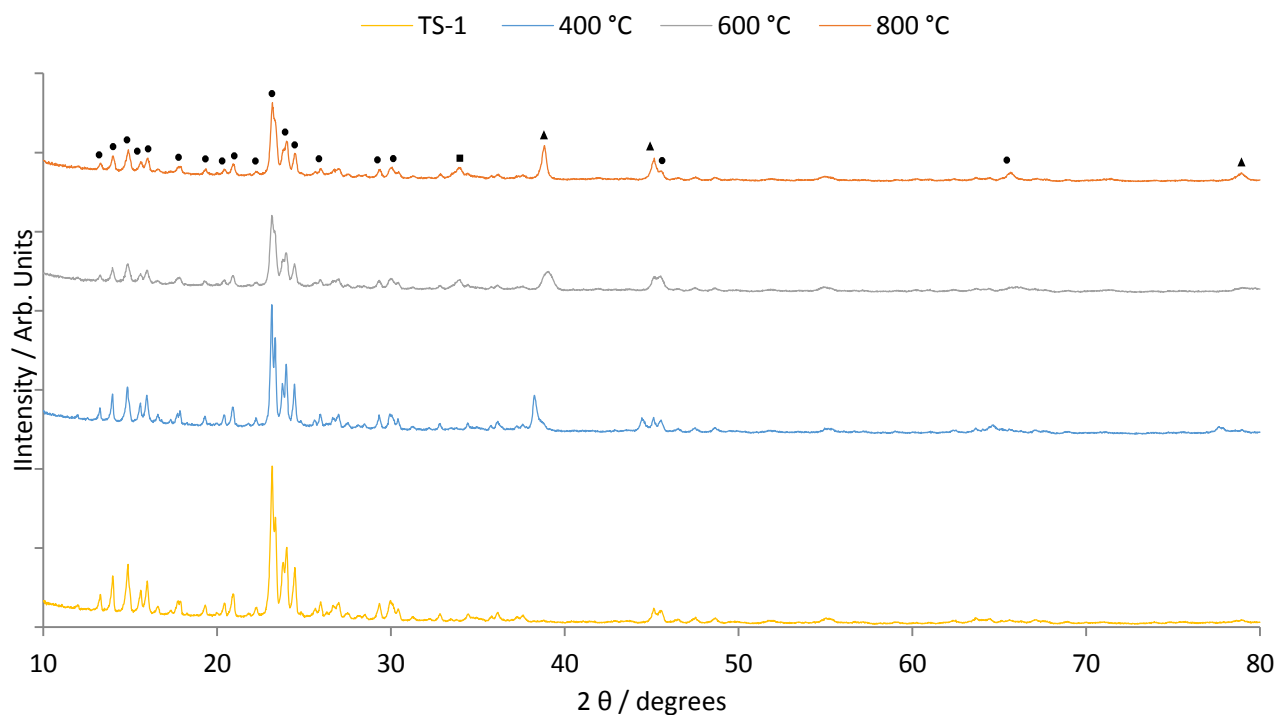
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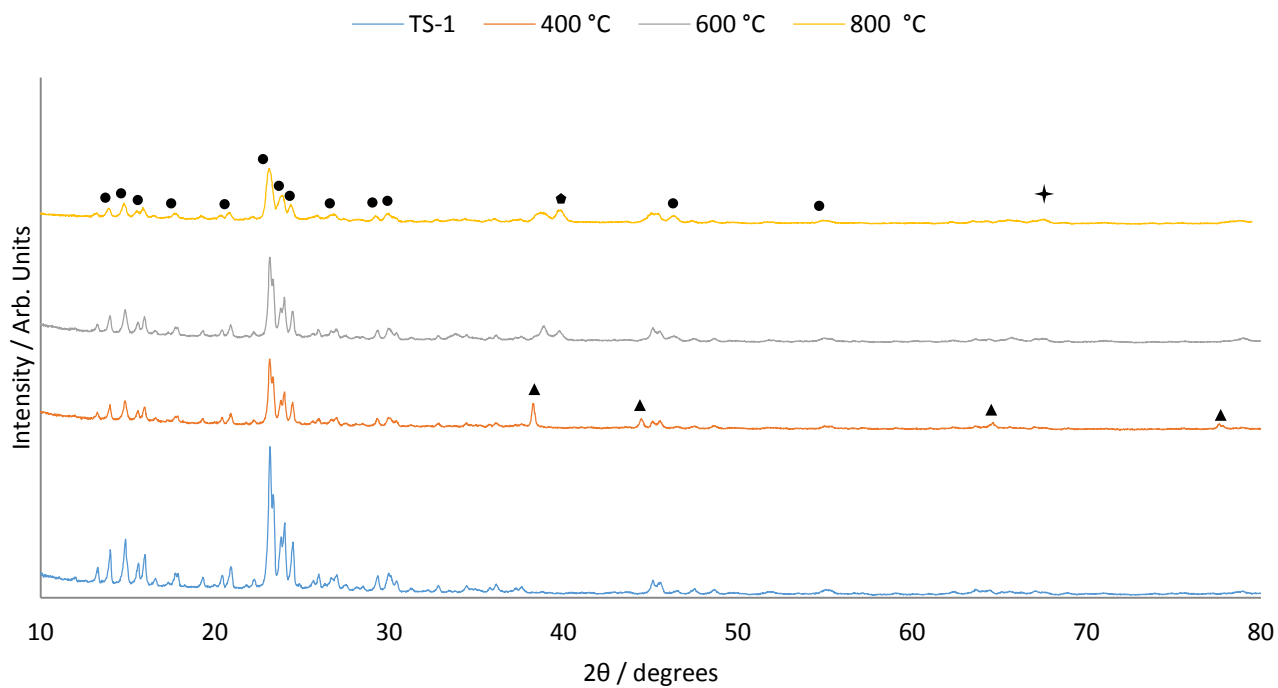
## Appendix 5.1



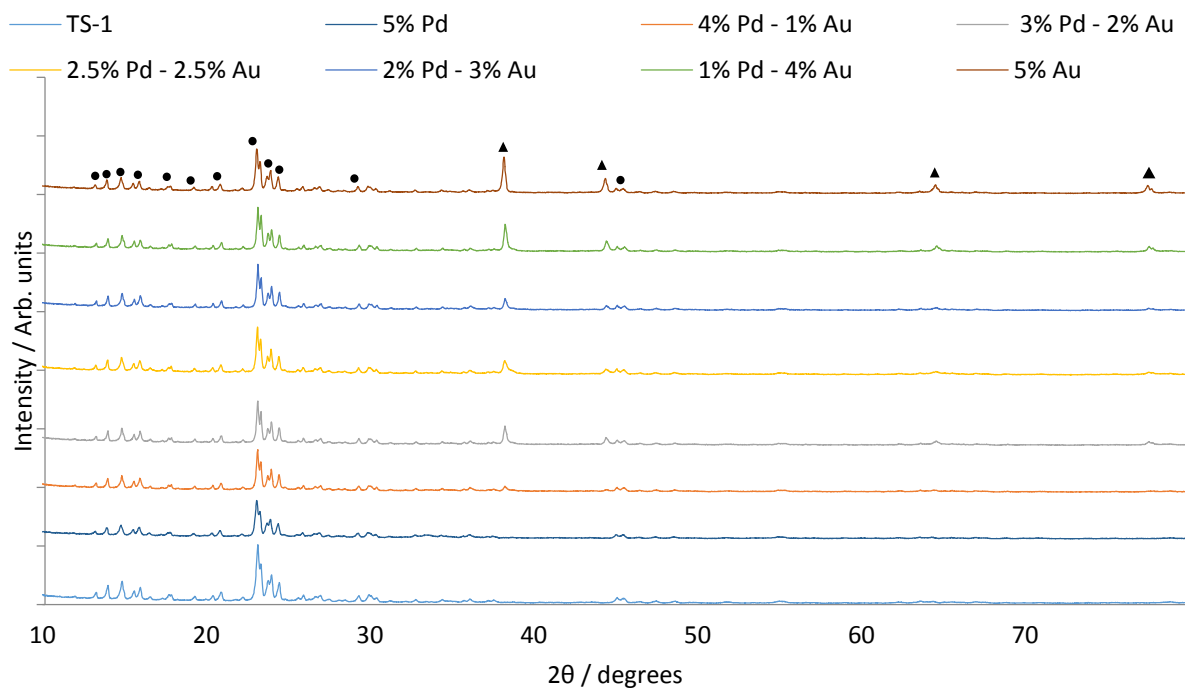
**Figure A1.** X-ray diffractograms of 5 wt. % Pd / TS-1 prepared by wet impregnation calcined at various temperatures (400 – 800 °C), 3 h, static air, ramp rate = 20 °C min<sup>-1</sup>. ●: TS-1 ; ■: PdO



**Figure A2.** X-ray diffractograms of 2.5 wt. % Au- 2.5 wt. % Pd / TS-1 prepared by wet impregnation, calcined at various temperatures (400 – 800 °C), 3h, static air, ramp rate = 20 °C min<sup>-1</sup>. ●: TS-1; ▲: Au; ■: PdO

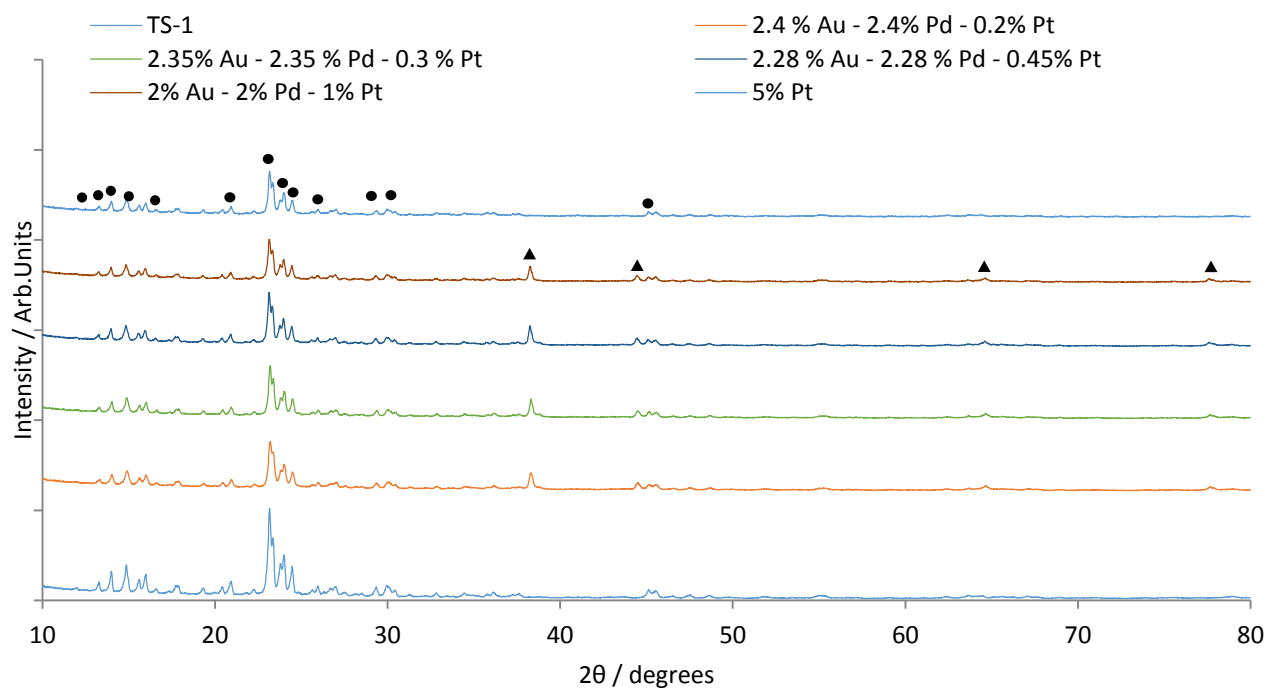


**Figure A3.** X-ray diffractograms of 2 wt. % Au- 2 wt. % Pd – 1 wt. % Pt / TS-1 prepared by wet impregnation, calcined at various temperatures (400 – 800 °C) 3 h, static air, ramp rate = 20 °C min<sup>-1</sup>. ●: TS-1; ▲: Au; ✦: Pt



**Figure A4.** X-ray diffractograms of 2.5 wt. % Au- 2.5 wt. % Pd / TS-1 prepared by wet impregnation calcined at 400 °C, 3 h, static air, ramp rate = 20 °C min<sup>-1</sup>. ●: TS-1; ▲: Au.





**Figure A5.** X-ray diffractogram of 5 wt. % Au-Pd-Pt / TS-1 and 5 wt.% Pt / TS-1 prepared by wet impregnation, calcined 400 °C in static air, ramp rate = 20 °C min<sup>-1</sup>. ●: TS-1; ▲: Au.

## Appendix 5.2.

**Table A.1.** Phase Identification of 5 wt. % Pd, AuPd and AuPdPt / TS-1 calcined at various temperatures (400 – 800 °C).

Catalyst	Calcination temperature / °C	Phase / %				
		TS-1	TiO <sub>2</sub>	PdO	Au	Pt
5 % Pd	400	98	2	-	-	-
	600	96	3	1	-	-
	800	93	5	2	-	-
2.5 % Au – 2.5 % Pd	400	96	3	-	1	-
	600	93	5	1	1	-
	800	91	6	1	2	-
2% Au – 2% Pd – 1% Pt	400	96	3	-	1	-
	600	93	5	-	1	1
	800	90	6	1	2	1

All catalysts calcined X °C, 3 h, 20 °Cmin<sup>-1</sup>, static air.

## Appendix 5.3.

**Table A.2.** XPS analysis of Pd / TS-1, AuPd / TS-1 and AuPdPt / TS-1 calcined at 400 -800 °C

Catalyst	Calcination Temperature / °C	Composition / At. %								Pd: Au	Pd : Pt	Ti <sup>8</sup> : Ti <sup>4</sup>	Si : Ti
		Pd 3d	Au 4f	Pt 4f	Cl 2p	O 1s	Si 2p	Ti 2p	C 1s				
Pd	400	1.14	-	-	0.75	61.62	34.3	0.33	1.86	-	-	1.49	103.9
	600	1.57	-	-	0.18	61.52	33.36	0.33	3.03	-	-	1.45	101.1
	800	1.01	-	-	-	61.52	34.27	0.43	2.06	-	-	1.95	79.7
AuPd	400	0.4	0.01	-	-	63.2	35.22	0.45	1.54	40	-	2.22	78.3
	600	0.21	0.03	-	-	62.52	35.32	0.54	1.39	7	-	2.25	65.4
	800	0.13	0.05	-	-	62.35	35.4	0.49	1.58	2.6	-	1.95	72.2
AuPdPt	400	0.28	-	0.27	0.57	59.08	103.79	0.37	0	0	1	1.5	88.2
	600	0.19	0.03	0.05	1.37	62.66	103.89	0.41	6.3	6.3	3.8	2.2	86.1
	800	0.12	0.07	0.03	-	62.92	103.65	0.54	1.7	1.7	4	1.2	65.3

All catalysts calcined X °C, 3 h, 20 °Cmin<sup>-1</sup>, static air.

**Table A.3.** XPS analysis of AuPdPt / TS-1 catalysts.

Catalyst	Composition / At. %								Pd: Au	Pd : Pt	Ti <sup>8</sup> : Ti <sup>4</sup>	Si : Ti
	Pd 3d	Au 4f	Pt 4f	Cl 2p	O 1s	Si 2p	Ti 2p	C 1s				
2.5 wt.% Au – 2.5 wt. % Pd	0.4	0.01	-	-	63.2	35.22	0.45	1.54	7	-	2.22	78.3
2.4 wt. % Au – 2.4 wt. % -0.2 wt. % Pt	0.34	0.01	0.01	0.34	59.31	36.11	0.45	3.44	34	34	1.33	80.24
2.35 wt. % Au – 2.35 wt. % -0.3 wt. % Pt	0.33	0.01	0.01	0.3	60.13	36.04	0.48	2.79	33	33	1.22	75.08
2.28 wt. % Au – 2.28 wt. % -0.44 wt. % Pt	0.32	0.01	0.01	0.26	59.05	35.34	0.42	4.62	33	32	1.22	84.14
2 wt. % Au – 2 wt. % Pd – 1 wt. % Pt	0.28	-	0.27	0.57	59.08	103.79	0.37	0	0	1	1.5	88.2

All catalysts calcined 400 °C, 3 h, 20 °Cmin<sup>-1</sup>, static air.

## 6. Conclusion and Future Work.

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### 6.1 .Conclusion.

As outlined in Chapter 1 the current, industrial, process for  $\text{H}_2\text{O}_2$  formation via the anthraquinone process offers a number of advantages including  $\text{H}_2$  selectivity. However the need to continually replace the organic solvent and the need for this process to be conducted on an industrial scale to be financially viable has led to a great deal of investigation into  $\text{H}_2\text{O}_2$  synthesis from molecular  $\text{H}_2$  and  $\text{O}_2$ .

The direct synthesis of  $\text{H}_2\text{O}_2$  represents a possible alternative to the anthraquinone process, however it presents some significant challenges. In particular the subsequent degradation of  $\text{H}_2\text{O}_2$  to  $\text{H}_2\text{O}$  via decomposition and hydrogenation, a requirement for any industrial application would of course be high selectivity towards  $\text{H}_2\text{O}_2$ , likely in excess of 95 %. The use of acidic reaction conditions<sup>1,2</sup> and acidified catalysts<sup>3-5</sup> has been shown previously to improve selectivity towards  $\text{H}_2\text{O}_2$  via reduction or complete inhibition of the subsequent degradation reactions.

Within this work the role of catalyst design has been investigated in improving catalyst activity towards  $\text{H}_2\text{O}_2$  synthesis (Chapter 3) through the investigation of Cs-exchanged tungstophosphoric acid, with varied Cs content, as an additive for catalysts already established for the direct synthesis of  $\text{H}_2\text{O}_2$ , in particular 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$ . The results presented within this chapter show some promise, with great improvement in catalytic activity towards  $\text{H}_2\text{O}_2$  observed. It has been demonstrated that the incorporation of Cs into the Keggin unit decreases the solubility of the heteropolyacid, with the concentration of W within the reaction solution decreasing from 1834 ppm when  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  is utilised as an additive to 240 ppm when  $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$  is used. However, as W is detected regardless of Cs incorporation it is possible to conclude that it is not possible to produce a totally insoluble material through the incorporation of Cs into the Keggin unit of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ .

As with W, Cs is detected regardless of the extent of its incorporation. A general trend can be observed where Cs concentration within the reaction solution increases as to a maximum of 183 ppm for the  $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ , further addition of Cs decreases the concentration of Cs

detected within the reaction solution, to a minimum of 95 ppm when  $\text{Cs}_3\text{HPW}_{12}\text{O}_{40}$  is used in addition to 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$ .

Furthermore it has been demonstrated that the use of  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  as an additive for 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  results in significant leaching of Pd from the support, with leaching of up to 30 % of the total Pd loading when  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  is used in addition to the catalyst. This coincides with the greatest catalytic activity towards  $\text{H}_2\text{O}_2$  synthesis with catalytic activity of  $301 \text{ mol}_{\text{H}_2\text{O}_2}\text{Kg}_{\text{cat}}^{-1}\text{h}^{-1}$ .

It is possible to conclude that both the 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  catalyst and  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  are unstable under the reaction conditions investigated and that in particular the presence of  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  promotes the leaching of Pd from the catalyst support, while no Au is detected in the reaction solution, suggesting that this metal is more stable than Pd.

Furthermore it is demonstrated that although the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts have no activity towards the direct synthesis of  $\text{H}_2\text{O}_2$  they are active towards the degradation of  $\text{H}_2\text{O}_2$ , with the activity of the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salt towards  $\text{H}_2\text{O}_2$  degradation correlating with Cs content. It is observed that the activity of the  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  parent material is  $35 \text{ mol}_{\text{H}_2\text{O}_2}\text{Kg}_{\text{cat}}^{-1}\text{h}^{-1}$  while that of  $\text{Cs}_3\text{HPW}_{12}\text{O}_{40}$  is  $213 \text{ mol}_{\text{H}_2\text{O}_2}\text{Kg}_{\text{cat}}^{-1}\text{h}^{-1}$  and this increase can be related, in part, to the amount of Cs leached from the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salt.

From investigation of the reusability of a physical mixture of 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  and  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  it is possible to conclude that only when the value of x in  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  is equal to 2.5 is the catalyst reusable. With a catalyst activity of  $188 \text{ mol}_{\text{H}_2\text{O}_2}\text{Kg}_{\text{cat}}^{-1}\text{h}^{-1}$  retained over two uses. However it has also been shown that Pd, Cs and W are all detected in the reaction solution post reaction and as such catalyst stability is a concern.

Finally comparison between catalytic activity towards  $\text{H}_2\text{O}_2$  synthesis when either  $\text{HNO}_3$ ,  $\text{H}_2\text{WO}_3$  or  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts are used in addition to 2.5 wt. % Au – 2.5 wt. % Pd /  $\text{TiO}_2$  suggests that the decrease in the reaction solution pH is not the only reason for improved  $\text{H}_2\text{O}_2$  synthesis activity. It is suggested that the presence of phosphate ions within the reaction solution improves  $\text{H}_2\text{O}_2$  stability and is responsible for the observed increase in catalytic activity towards  $\text{H}_2\text{O}_2$ . It is observed that as Cs incorporation decreases so does the stability of the  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salt and it is proposed that this results in an increase in the availability of  $\text{PO}_4^{3-}$  ions and improved  $\text{H}_2\text{O}_2$  stability.

It has been shown previously that the utilisation of exchanged tungstophosphoric acid as a support for metals active towards the synthesis of  $\text{H}_2\text{O}_2$  produces highly active catalysts<sup>6,7</sup>. In particular activity is considered to be relatively high when using conditions considered to be detrimental to  $\text{H}_2\text{O}_2$  synthesis, *i.e.* elevated temperatures and  $\text{H}_2\text{O}$  only solvents<sup>8,9</sup>. However both of these conditions are likely to be favoured by any industrial application due to the reduction in costs associated with ambient temperatures and a  $\text{H}_2\text{O}$  only solvent. The future investigation of supported Au-Pd catalysts in addition to Cs-exchanged heteropolyacids under these harsh conditions may make the direct synthesis of  $\text{H}_2\text{O}_2$  considerably more attractive. Although it is suggested that the low stability of  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  salts limit its application in any future use in the direct synthesis process in the liquid phase.

Chapters 4 and 5 investigate the ammoximation of cyclohexanone to cyclohexanone oxime via the in-situ synthesis of  $\text{H}_2\text{O}_2$ . As discussed previously the economic requirement of large scale  $\text{H}_2\text{O}_2$  synthesis ensures that costs for the ammoximation and other subsequent reactions that utilise  $\text{H}_2\text{O}_2$  as an oxidant can be particularly high and variable, both of these factors are clearly unattractive to industrial use. An attractive alternative to the current process, where preformed  $\text{H}_2\text{O}_2$  is added to the reaction mixture would be the *in-situ* synthesis of  $\text{H}_2\text{O}_2$  and ammoximation of cyclohexanone in a one-pot synthesis process.

Chapter 4 investigates the ability of monometallic Au, Pd and bimetallic Au-Pd catalysts supported on TS-1 to catalyse the formation of  $\text{H}_2\text{O}_2$  from  $\text{H}_2$  and  $\text{O}_2$ . The results are summarised in Table 6.1.

**Table 6.1.** The activity of TS-1 supported Au-, Pd- and Au-Pd catalysts towards the direct synthesis of  $\text{H}_2\text{O}_2$ .

Catalyst	Temperature / °C	Solvent	Productivity / $\text{mol}_{\text{H}_2\text{O}_2} \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$
5 wt. % Au /TS-1 <sup>(a)</sup>	2	$\text{H}_2\text{O}$ / MeOH	2
2.5 wt. % Au – 2.5 wt. % Pd /TS-1 <sup>(a)</sup>	2	$\text{H}_2\text{O}$ / MeOH	100
5 wt. % Pd/TS-1 <sup>(a)</sup>	2	$\text{H}_2\text{O}$ / MeOH	116
5 wt. % Pd/ TS-1 <sup>(a)</sup>	30	$\text{H}_2\text{O}$ / MeOH	26
5 wt. % Pd /TS-1 <sup>(b)</sup>	30	$\text{H}_2\text{O}$ / t-BuOH	60
5 wt. % Pd /TS-1 <sup>(b)</sup>	50	$\text{H}_2\text{O}$ / t-BuOH	12
5 wt. % Pd / TS-1 <sup>(b)</sup>	80	$\text{H}_2\text{O}$ / t-BuOH	7

**Reaction conditions:** <sup>(a)</sup> Catalyst (0.01 g), 580 psi,  $\text{H}_2$  /  $\text{O}_2$  = 0.525, 1200 rpm, 30 min, 5.6 g MeOH + 2.9 g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ), X °C. <sup>(b)</sup> Catalyst (0.01 g), 580 psi,  $\text{H}_2$  /  $\text{O}_2$  = 0.525, 1200 rpm, 30 min, 5.6 g t-BuOH + 2.9 g  $\text{H}_2\text{O}$  (66 wt. %  $\text{CH}_3\text{OH}$ ), X °C.

Firstly it is observed that no synergistic effect is observed between Au and Pd when using TS-1 as a support in a manner that has been reported by Hutchings and co-workers when using a variety of oxide supports including;  $\text{TiO}_2$ <sup>10</sup> and  $\text{SiO}_2$ <sup>11</sup>. Indeed the productivity of the 5 wt. % Pd / TS-1 catalyst is seen to be  $116 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ , while the productivity of the 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 catalyst is  $100 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ , when using a water/MeOH solvent at 2 °C. The activity of both the Pd / TS-1 and Au-Pd / TS-1 catalysts are comparable to that reported by Hutchings and co-workers for the 2.5 wt. % Au – 2.5 wt. % Pd / carbon catalyst ( $110 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ ), under comparable redaction conditions. It is possible to conclude that using TS-1 as a support for Au and Pd results in catalysts that have significant activity towards the direct synthesis of  $\text{H}_2\text{O}_2$ , under conditions optimised for this process.

It is further demonstrated that the use of a t-BuOH – water solvent offers greater rates of  $\text{H}_2\text{O}_2$  synthesis than MeOH – water at elevated reaction temperatures, with the activity of the 5 wt. % Pd / TS-1 catalyst observed to be 26 and  $60 \text{ mol}_{\text{H}_2\text{O}_2} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$  when MeOH – water and t-BuOH – water is used as the solvent at 30 °C. This is ascribed to increased  $\text{H}_2$  solubility in t-BuOH in comparison to MeOH. The application of a t-BuOH-water solvent system may warrant further investigation for its use in the direct synthesis of  $\text{H}_2\text{O}_2$  from  $\text{H}_2$  and  $\text{O}_2$ .

Chapter 4 further outlines the feasibility of the ammoximation of cyclohexanone via *in-situ* generation of  $\text{H}_2\text{O}_2$  using 5 wt. % Pd / TS-1 and investigates the role that the reaction conditions can play in improving both oxime yield and catalyst stability. It is demonstrated that there is some activity towards the ammoximation of cyclohexanone via *in-situ*  $\text{H}_2\text{O}_2$  synthesis is observed when utilising a 5 wt. % Pd / TS-1 catalyst. Table 6.2 summarises how the optimisation of reaction conditions can improve cyclohexanone oxime yield when utilising 5 wt. % Pd / TS-1, with the optimal reaction conditions highlighted in bold. Although optimal conditions have been established the effect of their combination on catalyst selectivity and cyclohexanone conversion have not been established. It is suggested that future work investigate the combination of the optimal reaction conditions in an attempt to improve the yield of cyclohexanone oxime.



**Table 6.2.** The effect of optimal reaction conditions on cyclohexanone oxime yield.

Temperature / °C	H <sub>2</sub> :O <sub>2</sub>	Catalyst Mass / g	H <sub>2</sub> O : t- BuOH	[Cyclohexanone] / mmol	[NH <sub>3</sub> ] / mmol	Time / min	Stirring Speed / rpm	Total Pressure / psi	Oxime Yield / %
<b>120</b>	0.525	0.05	0.5	1.3	1.3	90	1200	580	10
80	<b>1</b>	0.05	0.5	1.3	1.3	90	1200	580	7
80	0.525	<b>0.2</b>	0.5	1.3	1.3	90	1200	580	17
80	0.525	0.05	<b>0.5</b>	1.3	<b>1.3</b>	<b>90</b>	1200	<b>580</b>	4
80	0.525	0.05	0.5	<b>0.65</b>	1.3	90	1200	580	8
80	0.525	0.05	0.5	1.3	1.3	90	<b>800</b>	580	5

It has been shown that catalyst stability is an issue, in particular the presence of cyclohexanone,  $\text{NH}_3$  and a water containing solvent has been shown to result in the leaching of Pd from the support. Investigation in to the activity of leached Pd towards the ammoximation of cyclohexanone in the presence of TS-1 is observed to result in no additional formation of cyclohexanone oxime. It is suggested that the elevated temperatures and presence of basic reaction conditions, that is the presence of  $\text{NH}_3$ , ensures that any  $\text{H}_2\text{O}_2$  synthesised is unable to diffuse to the Ti(IV) sites present on the TS-1 support to be involved in the formation of hydroxylamine. However catalyst stability is of great concern and it is suggested that future work investigate methods of stabilising TS-1 supported catalysts.

Chapter 5 investigates catalyst design for the generation of  $\text{H}_2\text{O}_2$  *in-situ* and the subsequent ammoximation process. It is observed that the addition of Au to a Pd only catalyst in a 1 : 1 ratio does not result in an improvement in catalytic activity towards  $\text{H}_2\text{O}_2$  synthesis, that is no synergistic effect is observed between the two metals, as reported when utilising a number of other common supports<sup>11</sup>. Table 6.3 compares the catalytic activity of Au-Pd catalysts supported on TS-1 towards the direct synthesis of  $\text{H}_2\text{O}_2$  and the ammoximation of cyclohexanone.

**Table 6.3.** Activity of Au-Pd / TS-1 catalysts towards the direct synthesis of  $\text{H}_2\text{O}_2$  and the ammoximation of cyclohexanone.

Catalyst	Productivity / $\text{mol}_{\text{H}_2\text{O}_2}\text{kg}_{\text{cat}}^{-1}\text{h}^{-1}$ (a)	Oxime yield / % (b)
5 wt. % Au / TS-1	2	0.1
2.5 wt. % Au – 2.5 wt. % Pd / TS-1	100	2.8
5 wt. % Pd / TS-1	116	2

**Reaction Conditions:** (a) **Direct synthesis of  $\text{H}_2\text{O}_2$ :** Catalyst (0.01 g), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 5.6 g MeOH + 2.69 g  $\text{H}_2\text{O}$  (66 wt. % MeOH), 2°C.

(b) **Ammoximation of cyclohexanone:** Catalyst (0.05 g), cyclohexanone (0.13 g, 1.3 mmol),  $\text{NH}_3$  (0.08 g, 28 wt %, 1.3 mmol), total pressure 580 psi,  $\text{H}_2 / \text{O}_2 = 0.525$ , 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g  $\text{H}_2\text{O}$  (66 wt % t-BuOH), 80 °C.

It is observed that the greatest yield of cyclohexanone oxime is achieved utilising a 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 catalyst, despite the greater activity of the 5 wt. % Pd / TS-1 catalyst towards the direct synthesis of  $\text{H}_2\text{O}_2$ . It is suggested that by lowering the rate of  $\text{H}_2\text{O}_2$  synthesis it becomes similar to the rate of hydroxylamine formation and as such  $\text{H}_2\text{O}_2$  is utilised more selectively, in the formation of cyclohexanone oxime, rather than in the formation of  $\text{H}_2\text{O}$ .

Further investigation into TS-1 Au-Pd-Pt supported catalysts has shown that it is possible to improve the rate of  $\text{H}_2\text{O}_2$  synthesis through the introduction of small amount of Pt, while maintaining the Au : Pd ratio at 1 : 1. The results of Pt incorporation into a Au-Pd / TS-1

catalyst on catalytic activity towards the direct synthesis of H<sub>2</sub>O<sub>2</sub> and the ammoximation of cyclohexanone is summarised in Table 6.4.

**Table 6.4.** Activity of Au-Pd-Pt / TS-1 catalysts towards the direct synthesis of H<sub>2</sub>O<sub>2</sub> and the ammoximation of cyclohexanone.

Catalyst	Productivity / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> ( <i>a</i> )	Oxime yield / % ( <i>b</i> )
2.5 wt. % Au – 2.5 wt. % Pd / TS-1	100	2.8
2.4 wt. % Au – 2.4 wt. % Pd / 0.2 wt. % Pt / TS-1	167	1.6
2.35 wt. % Au – 2.35 wt. % Pd / 0.3 wt. % Pt / TS-1	149	2.16
2.4 wt. % Au – 2.4 wt. % Pd / 0.44 wt. % Pt / TS-1	124	2.2
2 wt. % Au – 2 wt. % Pd / 1 wt. % Pt / TS-1	69	5.6

**Reaction Conditions:** (*a*) **Direct synthesis of H<sub>2</sub>O<sub>2</sub>**: Catalyst (0.01 g), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g MeOH + 2.69 g H<sub>2</sub>O (66 wt. % MeOH), 2°C.

(*b*) **Ammoximation of cyclohexanone**: Catalyst (0.05 g), cyclohexanone (0.13 g, 1.3 mmol), NH<sub>3</sub> (0.08 g, 28 wt %, 1.3 mmol), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g H<sub>2</sub>O (66 wt % t-BuOH), 80 °C.

It can be seen that the incorporation of 0.2 wt% Pt can dramatically improve catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis, from 100 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> for the 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 catalyst to 167 mol<sub>H<sub>2</sub>O<sub>2</sub></sub>kg<sub>cat</sub><sup>-1</sup>h<sup>-1</sup> for the 2.4 wt. % Au – 2.4 wt. % Pd / 0.2 wt. % Pt / TS-1 catalyst. However the oxime yield decreases from 2.8 % to 1.6 % upon the incorporation of 0.2 wt. % Pt. Further incorporation of Pt decreases the catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis, while cyclohexanone oxime yield increases, to a maximum of 5.6 % for the 2 wt. % Au – 2 wt. % Pd / 1 wt. % Pt / TS-1 catalyst. It is suggested that, as shown previously with the 2.5 wt. % Au – 2.5 wt. % Pd / TS-1 catalyst, by lowering the rate of H<sub>2</sub>O<sub>2</sub> synthesis it is possible to ensure that H<sub>2</sub>O<sub>2</sub> is utilised more selectively and not degraded, either catalytically or by the reaction conditions to H<sub>2</sub>O and as such oxime yield is improved.

Investigation into the use of elevated calcination temperatures to improve catalyst stability has shown that it is possible to reduce the leaching of metals, in particular Pd, from the TS-1 support. However exposure to such elevated temperatures leads to the sintering of the metal nanoparticles and a resultant decrease in catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis and cyclohexanone ammoximation. Table 6.5 shows the effect of calcination temperature on catalytic activity towards H<sub>2</sub>O<sub>2</sub> synthesis and cyclohexanone ammoximation.

**Table 6.5.** The effect of calcination temperature on catalytic activity towards the direct synthesis of H<sub>2</sub>O<sub>2</sub> and the ammoximation of cyclohexanone.

Catalyst	Calcination temperature / °C	Productivity / mol <sub>H<sub>2</sub>O<sub>2</sub></sub> kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> <sup>(a)</sup>	Oxime yield / % <sup>(b)</sup>
5 wt. % Pd / TS-1	400	116	2.8
	600	25	0.72
	800	10	0
2.5 wt. % Au – 2.5 wt. % Pd / TS-1	400	100	2.8
	600	35	0.6
	800	30	0.2
2 wt. % Au – 2 wt. % Pd / 1 wt. % Pt / TS-1	400	69	5.59
	600	54	2.5
	800	42	1.6

**Reaction Conditions:** <sup>(a)</sup>**Direct synthesis of H<sub>2</sub>O<sub>2</sub>:** Catalyst (0.01 g), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g MeOH + 2.69 g H<sub>2</sub>O (66 wt. % MeOH), 2°C.

<sup>(b)</sup>**Ammoximation of cyclohexanone:** Catalyst (0.05 g), cyclohexanone (0.13 g, 1.3 mmol), NH<sub>3</sub> (0.08 g, 28 wt %, 1.3 mmol), total pressure 580 psi, H<sub>2</sub> / O<sub>2</sub> = 0.525, 1200 rpm, 30 min, 5.6 g t-BuOH + 2.69 g H<sub>2</sub>O (66 wt % t-BuOH), 80 °C.

It is observed that increasing calcination temperature results in a decrease in activity towards both H<sub>2</sub>O<sub>2</sub> synthesis and cyclohexanone ammoximation, regardless of catalyst composition. However it is also observed that the incorporation of Au into a Pd-only catalyst and Pt into a Au-Pd catalyst is able to offset the deleterious effect of calcination temperature on catalyst activity. Investigation by XRD shows that the incorporation of Au into a mono-metallic Pd catalyst, so that the ratio of Au : Pd is 1 : 1, is able to decrease the development of large Pd nanoparticles and a more pronounced effect is observed when Pt is introduced into a Au-Pd / TS-1 catalyst in Au : Pd : Pt ratio of 1 : 1 : 0.5. It is suggested that small Pd nanoparticles provide greater activity towards H<sub>2</sub>O<sub>2</sub> synthesis and as such by limiting the agglomeration of Pd it is possible to ensure some catalytic activity is retained.

In conclusion the utilisation of many metals active for the direct synthesis of H<sub>2</sub>O<sub>2</sub> supported on a commercial TS-1 support has led to improvement to the ammoximation reaction and it is suggested that through further catalyst design and process optimisation it may be possible for the ammoximation of cyclohexanone to cyclohexanone oxime via *in-situ* H<sub>2</sub>O<sub>2</sub> generation to present an alternative to the current industrial process.

## 6.2. Future Work.

A great deal of work published in the literature prior to and during this thesis has concerned improving catalytic selectivity towards  $\text{H}_2\text{O}_2$ , through the partial or complete inhibition of  $\text{H}_2\text{O}_2$  degradation pathways<sup>3 12</sup> (hydrogenation and decomposition). In all three chapters reported within this thesis it is recommended that further work concentrates on improving catalyst selectivity, particularly through catalyst design.

### 6.2.1 Improved use of metal.

By increasing the dispersion of metals active for the direct synthesis of  $\text{H}_2\text{O}_2$  it may be possible to produce a cheaper catalyst, with lower total metal loading. It has previously been shown that metal dispersion can be improved by the use of HCl during catalyst preparation<sup>13</sup>. Sankar *et.al.* have reported that the particle size distribution (PSD) for a Au-Pd /  $\text{TiO}_2$  catalyst prepared by conventional impregnation, the method used for catalyst preparation throughout this thesis, ranges from 10 nm to sub 1 nm with the mean particle size reported as 4.7 nm<sup>13</sup>. Despite this work focusing on the use of  $\text{TiO}_2$  as a support it is reasonable to assume that the PSD for the catalysts utilising a TS-1 support, such as those investigated in Chapters 4 and 5 would be similar.

Investigation of other catalyst preparation techniques that allow for better control over particle size such as; modified impregnation, sol-immobilisation and deposition precipitation may show some promise in improving catalytic activity towards  $\text{H}_2\text{O}_2$  synthesis as well as the ammoximation of cyclohexanone. By improving the dispersion of metals active for the direct synthesis of  $\text{H}_2\text{O}_2$  it may be possible to ensure that a greater proportion of the Ti (IV) sites present in the TS-1 support are available to produce hydroxylamine. It is suggested that by increasing dispersion of metals the diffusion path of  $\text{H}_2\text{O}_2$  from the metal nanoparticles to Ti (IV) sites is reduced.

It would also be of interest to determine how  $\text{H}_2\text{O}_2$  degradation, as well as  $\text{H}_2\text{O}_2$  synthesis, is altered by lowering the total metal loading of the catalysts studied within Chapter 3, in particular the 5 % Au- Pd /  $\text{TiO}_2$  catalyst.

### 6.2.2. Catalyst Stability.

The stability of catalysts for the ammoximation of cyclohexanone has been observed to be an issue, with leaching of Pd in particular observed to be of greatest concern. Further

investigation into methods to produce a stable catalyst is of the utmost concern although this issue may need a combination of catalyst and process design to overcome. It is suggested that by utilising a catalyst preparation technique that leads to a smaller mean particle size, such as modified impregnation and then exposing these catalyst to greater calcination temperatures it may be possible to retain a greater catalyst activity towards both the direct synthesis of  $\text{H}_2\text{O}_2$  and the ammoximation of cyclohexanone, in comparison to catalysts prepared by conventional impregnation, as well as improving catalyst stability.

The stability of the TS-1 support must also be determined as both the support and metals supported on it are key for the overall process and a greater understanding of both of these phases will be important for future development.

In comparison the activity to  $\text{H}_2\text{O}_2$  synthesis of Au-Pd catalysts prepared on  $\text{TiO}_2$  have been observed to be stable over two uses when  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  is utilised as an additive, despite the loss of Pd from the support. However, for any large scale use catalyst stability must be investigated over an extended reaction time and utilising a system more akin to that which will be used upon scale up of the process, be that a flow or slurry type reactor for example. Possibly a flow style reactor will allow for greater control of the reaction conditions, in particular flow rates of solvent over the catalyst and allow for on stream analysis of catalyst stability through the continual sampling of reaction solution and analysis of leached metal content. However, it is suggested that catalytic activity be monitored over multiple uses in a batch reactor to provide information on catalyst stability.

### 6.2.3. Catalyst synthesis technique.

The catalysts studied within this thesis are synthesised using a standard wet impregnation technique, as outlined in Chapter 2. However a variety of catalyst preparation techniques have been reported to produce catalysts active for the direct synthesis of  $\text{H}_2\text{O}_2$ , including modified impregnation<sup>13</sup>, sol-immobilisation<sup>14</sup> and physical grinding<sup>15</sup>. Although investigation of catalyst preparation should not be limited to these techniques it is recommended that they represent a good place to begin initial research. Principally into producing catalysts for the ammoximation of cyclohexanone via *in-situ*  $\text{H}_2\text{O}_2$  formation. It is suggested that the use of the modified impregnation technique to produce catalysts for the ammoximation of cyclohexanone may show some promise. Particularly if exposure to increased calcination temperatures is required to improve catalyst stability, as with the catalysts investigated within Chapter 5. Modified impregnation is known to produce a

catalysts with a narrow particle size distribution and a smaller mean particle size than conventional wet impregnation. By producing a greater population of smaller metal nanoparticles it is possible that a greater metal dispersion may be retained as catalysts are exposed to increased calcination temperatures and as such greater catalyst activity is preserved.

#### 6.2.4. The use of cheaper metals.

The replacement of Au with Sn has been studied by Hutchings and co-workers<sup>12</sup> for the direct synthesis of  $\text{H}_2\text{O}_2$  and is briefly touched upon within this thesis. In particular the ability of Cs-exchanged tungstophosphoric acid to promote a Pd-Sn /  $\text{TiO}_2$  catalyst for  $\text{H}_2\text{O}_2$  synthesis. Further investigation of these systems utilising exchanged heteropolyacids and non-precious metal containing catalysts would be of great interest. It is known that the by optimising both the Pd : Sn ratio and heat treatment cycle applied it is possible to produce a catalyst which is totally selective towards  $\text{H}_2\text{O}_2$ , that is there is no activity towards the degradation of  $\text{H}_2\text{O}_2$ . In this way it is possible to limit the degradation of  $\text{H}_2\text{O}_2$  to that observed for the heteropolyacid only. It is suggested that future work investigate the activity of a catalyst that is totally selective towards  $\text{H}_2\text{O}_2$  when used in utilisation with  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and its Cs-exchanged salts.

While for the '*in-situ*' ammoximation reaction only precious metals (Au, Pd and Pt) were studied. However the use of cheaper base metals as replacements for one or more of the precious metals may be of great interest to any industrial application particularly if catalyst activity can be retained.

#### 6.2.5. Particle composition.

It is known that when Au-Pd catalysts are prepared by impregnation, on a range of oxide supports it is possible to form Au-Pd alloyed nanoparticles with a bimodal distribution of particle size. The morphology of these Au-Pd particles have been observed to often exhibit a core-shell structure, with a Pd-rich shell and Au-rich core.<sup>16-18</sup> Often the smaller particles are found to be Pd rich and the larger ones Au rich. It has been shown that when supported on  $\text{TiO}_2$  the addition of Pt to Au-Pd results in a significant narrowing of the particle size distribution<sup>19</sup>. It would be of great interest to determine if this effect is also observed when catalysts are prepared on TS-1. In addition to this it would be of interest to truly determine whether or not alloying between Au and Pd is observed in these bi-metallic catalysts is

responsible for the improvement in catalytic activity towards cyclohexanone oxime formation, or if there is another means by which improvement occurs. Furthermore it has been suggested that the role of Pt is to enhance the surface Pd : Au ratio when utilising CeO<sub>2</sub> as a support for these Au-Pd-Pt catalysts<sup>20</sup>. A similar improvement is observed for the AuPdPt / TS-1 catalysts however it is unclear if the increase in Pd : Au surface ratio is due to an enhancement of Au-core Pd-shell morphology or simply due to improved dispersion of the metal. It is suggested further work be conducted to determine the role Pt plays in promoting catalytic activity when using TS-1 as a support.

#### 6.2.6. Determine the activity of TS-1 supported catalysts towards the ammoximation of other substrates.

It is known that the combination of H<sub>2</sub>O<sub>2</sub> and TS-1 is able to catalyse a number of oxidation reactions, including alkanes, alkenes, alcohols and aromatics under mild conditions. These reactions often require the continuous addition of H<sub>2</sub>O<sub>2</sub> and a significant proportion of the process costs are associated with the transportation and storage of preformed H<sub>2</sub>O<sub>2</sub>. Application of in-situ H<sub>2</sub>O<sub>2</sub> synthesis for the various oxidation processes provides a more environmentally friendly, cheaper and safer alternative to the use of pre-formed H<sub>2</sub>O<sub>2</sub>. Particularly if H<sub>2</sub> generation can be achieved via electrolytic splitting of water. It is suggested that the approach utilised within Chapters 4 and 5 for the ammoximation of cyclohexanone should first be investigated for other ketone substrates, such as 2-butanone, to determine the efficiency of the one-pot approach and then expanded to alcohols and other substrates if possible.

#### 6.2.7. Determine the role of phosphate present in Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> salts in improving the stability H<sub>2</sub>O<sub>2</sub>.

It was postulated in Chapter 3 that the improvement in H<sub>2</sub>O<sub>2</sub> activity observed when Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> salts are used in conjunction with 2.5 wt. % Au – 2.5 wt. % Pd / TiO<sub>2</sub> is not solely due to the decrease in reaction solution pH but also due to improved stability of H<sub>2</sub>O<sub>2</sub> through the presence of PO<sub>4</sub><sup>3-</sup>, a known H<sub>2</sub>O<sub>2</sub> stabilising agent<sup>21</sup>. It is suggested that further work be carried out to investigate the availability of PO<sub>4</sub><sup>3-</sup> when utilising Cs<sub>x</sub>H<sub>3-x</sub>PW<sub>12</sub>O<sub>40</sub> salts in a polar medium and how the incorporation of Cs into the Keggin cage structure of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> can limit the availability of PO<sub>4</sub><sup>3-</sup>.



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